

IN
1
A5
Vol. 78
1928
N/c

Transactions

PROCEEDINGS

OF THE

INSTITUTE OF METALS DIVISION

1928

AMERICAN INSTITUTE OF MINING
and Petroleum
AND METALLURGICAL ENGINEERS //

(INCORPORATED)

min-eng
7

PAPERS PRESENTED BEFORE THE DIVISION, AT DETROIT, MICH.,
SEPT. 19-24, 1927, AND NEW YORK, FEB. 20-23, 1928.

NEW YORK, N. Y.
PUBLISHED BY THE INSTITUTE
29 WEST 39TH STREET
NEW YORK CITY

Notice

This volume is the second of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with non-ferrous metals and includes all papers presented at the Detroit Meeting, Sept. 19-24, 1927, and the New York Meeting, Feb. 20-23, 1928.

The series is a continuation of the previous publications and proceedings of the Institute of Metals Division, which are as follows:

1908-1911 *Transactions* of the American Brass Founders' Association.

1912-1916 *Transactions* of the American Institute of Metals.

1917 *Journal* of the American Institute of Metals.

1918-1926 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes Nos. 60, 64, 69, 70, 71 and 73.

1927 *PROCEEDINGS* of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

1928 *PROCEEDINGS* of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

COPYRIGHT, 1928, BY THE
AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

[INCORPORATED]

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

CONTENTS

	PAGE
Officers and Committees.	5

PAPERS

Twinning in Metals (Annual Lecture). By C. H. Mathewson	7
Physical Characteristics of Commercial Copper-zinc Alloys. By W. H. Bassett and C. H. Davis (With Discussion)	55
Nickel and Monel Metal, with Especial Reference to Annealing. By C. A. Crawford.	74
Wrought Zinc. By C. S. Trewin	95
Commercial Forms and Applications of Aluminum and Aluminum Alloys. By P. V. Faragher	99
Some Aspects of the Commercial Manipulation of Aluminum. By C. F. Nagel, Jr. (With Discussion)	127
Machining Aluminum. By R. L. Templin (With Discussion).	149
Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. By E. H. Dix, Jr. and A. C. Heath, Jr. (With Discussion)	164
Heat Treatment of Aluminum-silicon Alloys. By R. S. Archer, L. W. Kempf and D. B. Hobbs (With Discussion).	198
Condition of Thorium in Thoriated Tungsten Filament. By Ancel St. John (With Discussion).	228
X-ray Analysis of Plastic Deformation of Zinc. By T. A. Wilson and S. L. Hoyt (With Discussion).	241
Quantitative Spectrum Analysis. By F. Twyman and D. M. Smith (With Discussion).	280
The Production of Metallic Single Crystals. By J. A. M. van Liempt (With Discussion).	307
Ternary Systems of Lead-antimony and a Third Constituent. By R. A. Morgen, L. G. Swenson, F. C. Nix and E. H. Roberts (With Discussion).	316
A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders. By Carl E. Swartz (With Discussion).	352
Some Peculiar Results in Hardness Tests of Lead-antimony Alloys. By L. O. Howard (With Discussion).	369
The Cause of Translation Striae and Translation Strain-hardening in Crystals. By M. J. Buerger (With Discussion).	375
Grain Growth in Metals Caused by Diffusion. By Floyd C. Kelley (With Discussion).	390
Interatomic Forces in Metals and Alloys. By Robert F. Mehl (With Discussion).	405
Twinning in Copper and Brass. By Albert J. Phillips (With Discussion).	429
Twinning in Beryllium, Magnesium, Zinc and Cadmium. By C. H. Mathewson and A. J. Phillips.	445
Twinning in Ferrite. By L. W. McKeehan (With Discussion)	453
Magnesium—Its Etching and Structure. By H. B. Pulsifer (With Discussion).	461
Manganese in Non-ferrous Alloys. By M. G. Corson (With Discussion).	483

	PAGE
Alpha Phase Boundary of the Copper-nickel-tin System. By Wm. B. Price, C. G. Grant and A. J. Phillips (With Discussion)	503
Distribution of Tensile Strength in Hard Drawn Copper Wire. By Frank W. Harris (With Discussion).	518
Application of a High-vacuum Induction Furnace to the Study of Gases in Metals. By P. H. Brace and N. A. Ziegler (With Discussion)	544
Corrosion of Metals as Affected by Time and by Cyclic Stress. By D. J. McAdam, Jr. (With Discussion)	571
Aluminum-beryllium Alloys. By R. S. Archer and W. L. Fink (With Discussion).	616
Behavior of Molybdenum as Resistor in the Electric Furnace. By Henry J. Miller and Marcella Lindeman	647

SECONDARY METALS

Non-ferrous Secondary Metals Recovered in the United States. By J. P. Dunlop (With Discussion)	660
Sampling and Evaluating Secondary Non-ferrous Metals. By T. A. Wright (With Discussion).	672
Classification and Preparation of Non-ferrous Scrap Metals and Alloys. By H. F. Seifert	694
Modern Non-ferrous Secondary Metal Producer. By Don C. Blackmar (With Discussion).	700
The Contamination of Metal Scrap, Its Effect on the Value, and Suggested Means of Control. By Carl O. Thieme (With Discussion)	711
Metal Recovery from Bronze Foundry Slags. By E. R. Darby (With Discussion).	721
Remelting Secondary Aluminum. By T. D. Stay, D. B. Hobbs and H. O. Burrows.	726

PRECIOUS METALS

Manufacture of Sterling Silver and Some of Its Physical Properties. By Robert H. Leach and C. H. Chatfield (With Discussion).	743
The Platinum Metals and Their Alloys. By Frederic E. Carter (With Discussion).	759
Gold, Silver, Copper Alloys. By Frederic E. Carter (With Discussion)	786
Use of the Noble Metals for Electrical Contacts. By E. F. Kingsbury (With Discussion).	804
INDEX	825

A. I. M. E. OFFICERS AND DIRECTORS

For the Year Ending February, 1929

President, GEORGE OTIS SMITH, Washington, D. C.
 Past President, SAMUEL A. TAYLOR, Pittsburgh, Pa.
 Past President, E. DeGOLYER, New York, N. Y.
 First Vice-president, W. H. BASSETT, Waterbury, Conn.
 Treasurer, KARL EILERS, New York, N. Y.
 Secretary, H. FOSTER BAIN, New York, N. Y.
 Assistant Secretary, THOMAS T. READ, New York, N. Y.

VICE-PRESIDENTS

BIRCH O. MAHAFFEY, St. Louis, Mo.
 CARL A. MEISSNER, New York, N. Y.
 HENRY KRUMB, Salt Lake City, Utah.

F. JULIUS FOHS, New York, N. Y.
 W. H. BASSETT, Waterbury, Conn.
 GEORGE D. BARRON, New York, N. Y.

DIRECTORS

L. K. ARMSTRONG, Spokane, Wash.
 H. A. GUESS, New York, N. Y.
 W. SPENCER HUTCHINSON, Cambridge, Mass.
 HARVEY S. MUDD, Los Angeles, Calif.
 RENO H. SALES, Butte, Mont.
 FRANK H. CROCKARD, Woodward, Ala.
 J. O. ELTON, Salt Lake City, Utah.
 DANIEL C. JACKLING, San Francisco, Calif.

DAVID LEVINGER, Chicago, Ill.
 RICHARD PETERS, JR., Philadelphia, Pa.
 HERMAN C. BELLINGER, New York, N. Y.
 KARL EILERS, New York, N. Y.
 H. G. MOULTON, New York, N. Y.
 J. V. W. REYNOLDERS, New York, N. Y.
 ROBERT E. TALLY, Jerome, Ariz.

Counsel, DOUGLAS, ARMITAGE AND McCANN, New York, N. Y.

Officers and Committees of the Institute of Metals Division

ZAY JEFFRIES, *Vice-chairman*

S. SKOWRONSKI, *Chairman*

WILLIAM M. CORSE, *Secretary*

Executive Committee

J. R. FREEMAN, JR., *Local Section*
 R. S. ARCHER, *Non-ferrous Data Sheets*
 EDGAR C. BAIN, *Journal Committee*
 SAM TOUR, *Papers Committee*
 H. C. JENNISON, *Membership Committee*

G. E. JOHNSON
 P. D. MERICA
 L. W. SPRING
 F. L. WOLF

Local Section Committee

R. J. ANDERSON, Cincinnati
 G. H. CLAMER, Philadelphia

J. R. FREEMAN, JR., *Chairman*
 R. L. DOWDELL, Minneapolis
 W. A. SCHEUCH, Chicago

R. S. WILLIAMS, Boston
 R. F. WOOD, New York

Papers Committee

E. H. DIX, JR.—Aluminum
 H. A. BEDWORTH—Brass

SAM TOUR, *Chairman*
 E. R. DARBY—Bronze
 W. K. FRANK—Bronze
 R. L. SUHL—Nickel

C. S. WITHERELL—Copper
 F. W. HARRIS—Copper

H. M. ST. JOHN—Foundry Metallurgy

R. S. DEAN—Theoretical Metallurgy

Research Committee

R. S. ARCHER
 W. H. BASSETT
 WILLIAM CAMPBELL
 WILLIAM M. CORSE

PAUL D. MERICA, *Chairman*
 H. W. GILLETT
 S. L. HOYT
 M. A. HUNTER
 C. H. MATHEWSON

V. SKILLMAN
 A. E. WHITE
 H. M. WILLIAMS

Data Sheet Committee

T. S. FULLER

R. S. ARCHER, *Chairman*
 C. H. MATHEWSON
 F. L. WOLF

J. STRAUSS

Annual Lecturer Committee

GEORGE K. BURGESS

ZAY JEFFRIES, *Chairman*
 WILLIAM CAMPBELL
 WILLIAM M. CORSE

G. H. CLAMER

Journal Committee

W. A. COWAN
 E. H. DIX, JR.
 W. H. FINKELDEY

EDGAR C. BAIN, *Chairman*
 S. L. HOYT
 JAMES T. KEMP
 A. B. KINZEL
 H. S. RAWDON

H. M. ST. JOHN
 E. E. THUM
 SAM TOUR



Digitized by the Internet Archive
in 2023

Twinning in Metals

By C. H. MATHEWSON,* NEW HAVEN, CONN.

(Institute of Metals Division Lecture, † 1928)

MICROSCOPIC metallography has been exploited quite well enough to bring about a very general understanding that the typical metal or alloy is composed of minute crystalline particles blended into a coherent microstructural mosaic. One does not have to be a specialist in metallography to realize that the properties of such an aggregate are essentially a summation in appropriate form of individual effects derived from the shape, size, placement or orientation and cohesive characteristics of the component particles.

It is clearly of great importance to consider the various forms of discontinuity which may occur at the boundaries between these crystalline particles. When a number of particles each possessing the same orderly arrangement of atoms are brought together into a close-fitting system of purely haphazard contacts, not unlike a handful of snowflakes compacted into a snowball, the particles are said to possess random orientation. There are no generally accepted views concerning the arrangement of the atoms or the constitutional reaction between atoms where one crystal meets another, but these contact regions are characterized by strength rather than weakness and it is customary to require the presence of many rather than few boundaries in preparing metal for useful service.

Under certain circumstances all of the particles in a metal may be nearly alike in orientation. Other general tendencies of orientation may be associated with particular forms of mechanical and thermal treatment.

In contrast with these cases of fortuitous or statistical diversity of orientation, we often find adjacent particles united along a plane which possesses a grouping of atoms belonging equally well to both structures. This, of course, determines a fixed relationship between the two orientations and it is always possible to derive one from the other by some form of rotation or reflection prescribed by the symmetry of the crystal structure under consideration. Particles united in this manner are known as twin crystals although the term refers to the form of association rather than the number of individuals concerned.

* Professor of Metallurgy, Yale University.

† New York Meeting, February, 1928.

Twinning, in common with other features pertaining to the crystalline habit of minerals, is of value in identifying them and has been thus far considered chiefly from that point of view. In the field of metallurgy it is important as a form of structure alteration which appears to be vitally concerned in many metallurgical processes. In approaching this subject I have first sought to discover the extent to which twinning has been observed in the general list of metals.

TWINNING IN THE COMMON METALS

All of the metals which come frequently into the hands of every observer and may therefore be termed common metals—namely, copper, silver, gold, iron, aluminum, zinc, lead, tin, nickel, and platinum—are quite definitely known to occur in the form of twinned crystals, with the possible exception of aluminum, after an appropriate life history in which stress and heat treatment are chiefly instrumental.

In some of these cases, twinning was recognized in native metals or in special preparations, *e. g.*, isolated crystals, long before the day of wholesale examination of metal structures by the methods of the metallographic laboratory. Thus, crystals of native gold and copper twinned along an octahedral plane are described by Dana¹ and the large hand-books² tell us that twinning of the same form has been observed in natural crystals of the other face-centered cubic metals, silver, lead, platinum (and iridium).

The ordinary microstructures developed in metals by polishing and etching do not lend themselves readily to the quantitative interpretation of crystallographic characteristics, aside from the size of the crystalline grains, but they do permit instant recognition of the twin relationship in so far as this is revealed by the customary rectilinear trace of the twinning plane in the surface under observation and the uniform coloration of polysynthetic twin lamellae, which often occur in great profusion. These structural features give character and individuality—in fact, an impressionistic cubist appearance quite evident in Fig. 1—to the familiar photomicrographs of hot-worked or cold-worked and annealed copper, silver, gold, and their alpha solutions.

Copper and Alpha Brass

Although it is generally assumed that recrystallized copper and alpha brass twin along octahedral planes, Tammann and Meyer³ report twin-

¹ E. S. Dana: Textbook of Mineralogy, 3d Ed., 1922, 173, 350 and 353. John Wiley & Sons, Inc., New York.

² E. S. Dana: System of Mineralogy, 6th Ed. 1892. John Wiley & Sons, Inc., New York.

P. H. Groth: Chemische Kristallographie, Part I, 1906. W. Engelmann, Leipzig.

³ G. Tammann and H. H. Meyer: Die Aenderung der Kristallitenorientierung bei der Rekristallisation von Kupfer. *Zeitschr. für Metall.* (1926) **18**, 176.

ning along trapezohedral planes of form $\{211\}$ in their samples of recrystallized copper, some of which were prepared by mildly cold-working sections taken parallel to the cooling surface of a casting and then annealing for a period of one hour at a temperature of 750° to 800° C. Moreover, quite recently C. F. Elam,⁴ in an X-ray examination of what appeared to be well-marked twin bands in a sample of native copper, could find no important crystal plane or direction common to both parts of the structure.

No crystallographic measurements sustaining the first assumption were discovered, although it can scarcely be doubted that others in common with observers in the Hammond Laboratory have found slip

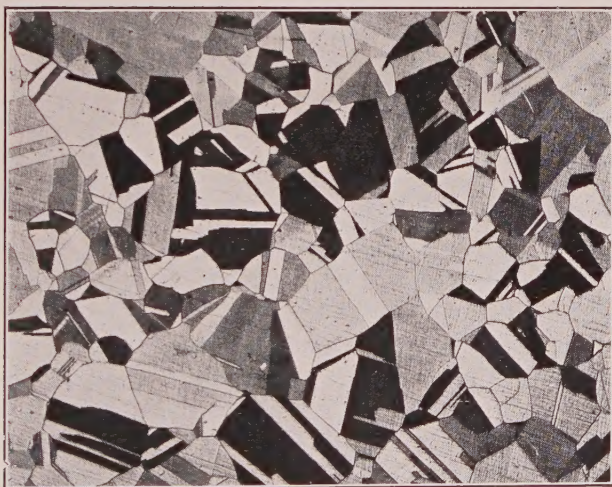


FIG. 1.—TWINS IN ALPHA BRASS.

bands, universally held to follow the octahedral planes, parallel and otherwise appropriately related to the twin bands in strained samples of annealed copper or alpha brass. In order to test this assumption further, A. J. Phillips⁵ prepared samples of coarse-grained copper and 70:30 brass cut and polished on two planes intersecting at right angles so as to permit measurement of the angles between two, three, or even four hypothetical twinning planes in a given crystal and the edge in each surface plane. The poles of these planes were then located in a stereographic projection and the distances between planes were measured. The two copper crystals and eight brass crystals investigated all gave measurements approximating to the nearest degree of arc the correct angles, 70° , $31'$, $44''$ or 109° , $28'$, $16''$ between octahedral twinning planes, and

⁴ C. F. Elam: Banded Structure in Aluminum and Copper. *Nature* (1927) **120**, 259.

⁵ A. J. Phillips: Twinning in Copper and Brass. See p. 429.

furthermore a similar analysis of internal twin bands in both parts of a twinned copper or brass crystal left no doubt that the twinning axis was perpendicular to the observed composition plane.

This work proves that twinning in recrystallized copper or alpha brass sometimes if not always occurs parallel to an octahedral plane around an axis normal to this plane.

Steel and Iron

It is well known that the austenitic steels, which may be considered to represent gamma iron, yield twinned structures which are scarcely to be distinguished from the familiar copper and brass structures. This twinning has been observed in plain carbon steel in the form of a record left after etching at a suitably elevated temperature,⁶ although it is not possible to hold the metal wholly in the gamma condition on cooling. Osmond and Cartaud⁷ affirm that "the octahedral faces are at the same time planes of translation, planes of twinning, and planes of junction" in gamma iron and this applies to twins produced by simple deformation as well as to those produced by annealing after deformation.

Twinning in ferrite, or body-centered cubic iron, has been precisely described in a recent paper by McKeehan⁸ who, by analyzing the specular reflection from bright cube faces left by etching in dilute nitric acid, finds the twin crystal united along planes of form $\{211\}$ in such manner that a common orientation would result by rotating one part through 60° around an axis of form $[111]$; *viz.*, one of the axes of threefold symmetry. S. Tamura⁹ within the past year has reported an occurrence of occasional bands in the ferrite grains of wrought iron and mild steel under the name "pseudo twins," not intended to define them specifically as pseudomorphs of earlier bands in austenite, but to emphasize his impression that metals which crystallize in the body-centered cubic lattice seldom, if ever, form annealing twins.

The twins observed in Armco iron wire by McKeehan were produced probably as a result of incidental mechanical disturbance during the process of growing a crystal of alpha iron by causing it to feed on a reserve of transforming gamma iron supplied continuously by uniform progression of the wire through a suitably heated zone. Although the wire was cold-worked to begin with, the temperature conditions set up in the process would appear to require that these twins be regarded as

⁶ M. A. Baykoff: Sur la Structure des Aciers aux Températures Élevées. *Rev. de Met.* (1909) **6**, 829.

⁷ F. Osmond and G. Cartaud: The Crystallography of Iron. *Jnl. Iron and Steel Inst.* (1906) **71**, 444.

⁸ L. W. McKeehan: Twinning in Ferrite. See p. 453.

⁹ S. Tamura: Notes on Pseudo-Twinning in Ferrite. *Jnl. Iron and Steel Inst.* (1927) **115**, 747.

annealing twins rather than mechanical or deformational twins, following the form of classification so generally adopted by participants in this field of research. I question the inherent value of this distinction and look forward to the time when sufficient evidence is available to prove the origin of all twin structures. At present it may be confidently asserted that twinning, quite in common with recrystallization, never occurs as a result of annealing metals which have passed tranquilly from the liquid to the solid state but is induced by strain and that recrystallization and twinning are mutually reactive at some stage of the combined deformational and annealing process. Thus all twins may be of mechanical origin and outstanding differences due to their original dimensions and their subsequent behavior on annealing.

Neumann Bands

About twenty-five years ago O. Mügge¹⁰ made a careful crystallographic study of the characteristic lamellae, commonly known as Neumann bands, which ordinarily appear when iron is deformed by sudden impact. An earlier observation by Linck¹¹ that these lamellae followed planes of form $\{211\}$ was confirmed by Mügge who observed the directions of the lamellae on cubic cleavage planes and measured the angles of contact between the intersecting surfaces. A complete interpretation of the results was offered, according to which twinning along the plane (112) brought about a transformation of (010) , (100) or (001) planes into $(\bar{1}\bar{1}2)$, $(\bar{1}12)$ or (110) planes, respectively.

Some twenty years later, Mügge¹² pointed out that on the basis of the twinning characteristics previously established, alpha iron would have to crystallize in the body-centered form of the cubic lattice, as has been amply demonstrated by the modern X-ray methods.

In spite of the definite outcome of this pioneering work, the Neumann bands in iron have given rise to a long-continued controversy. Howe gave elaborate attention to this subject in a long chapter of his well known treatise¹³ under the caption, "The Neumann Bands or Mechanical Twins in Ferrite," which fairly reveals his position in the matter. He demonstrated that these bands habitually occur parallel to planes of form $\{211\}$ (quite in agreement with Osmond, Mügge, Linck and others) but no means of detecting the exact change of orientation across the provisional twinning plane could be found and hence complete proof of crystallographic twinning could not be deduced.

¹⁰ O. Mügge: Über neuere Strukturflächen an den Krystallen der gediegenen Metalle. *Jahrb. für Min.* (1899) **2**, 55.

¹¹ *Zeitschr. für Kristall.* (1892) **20**, 209.

¹² O. Mügge: Struktur und einfache Schiebungen des Eisens. *Zeitschr. anorg. Chem.* (1922) **121**, 68.

¹³ H. M. Howe: *The Metallography of Steel and Cast Iron*. 1916. McGraw-Hill Book Co., Inc., New York.

Conflicting points of view are emphasized by the rather recent work of O'Neill¹⁴ and Rosenhain and McMinn¹⁵ on this general subject. The first of these authors confirms the earlier location of a provisional twinning plane {211} and presents interesting arguments as to the inherent probability of twinning on the ground of a simple translatory mechanism which would readily yield twinned structures. On the other hand, Rosenhain and McMinn were unable to trace slip bands through Neumann lamellae in conformity with the requirements of twinning as seen by them. The present uncertainty concerning the nature of slip bands in ferrite and their unfavorable form would appear to affect seriously an analysis of this sort.

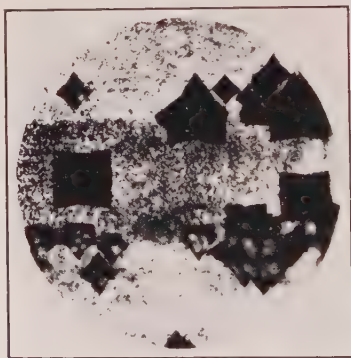


FIG. 2.—ETCHING FIGURES WITHIN AND ADJACENT TO A NEUMANN BAND IN SILICON-FERRITE. (HARNECKER AND RASSOW.)

A striking illustration of the condition which would under favorable circumstances be revealed by slip bands, namely, change of orientation in passing from crystal to twin band, is furnished by the etching figures around and within the Neumann band shown in Fig. 2 from an interesting study of Neumann bands in iron containing 0.6 per cent. nickel and 1.3 per cent. phosphorus by Harnecker and Rassow.¹⁶

The weight of evidence seems to favor the conception that Neumann bands are twin lamellae but the attendant controversy has clearly reached a stage in which no amount of argument founded upon any set of circumstances less vital than the rigorous determination of the crystal structure within and adjacent to the bands can prevail.

¹⁴ H. O'Neill: Deformation Lines in Large and Small Crystals of Ferrite. *Jnl. Iron and Steel Inst.* (1926) **113**, 417.

¹⁵ W. Rosenhain and J. McMinn: The Plastic Deformation of Iron and the Formation of Neumann Lines. *Proc. Roy. Soc.* (1925) **108**, 231.

¹⁶ K. Harnecker and E. Rassow: Aetzfiguren und Zwillingsbildungen in Eisen. *Zeitschr. für Metall.* (1924) **16**, 312.

Aluminum

Aluminum seems exceptionally shy in disclosing evidence of twinning. According to C. F. Elam,¹⁷ banded structures are rarely encountered and in two cases investigated by means of the X-rays the plane of junction was not related to the crystal structure of either hypothetical twin component. The crystals did appear to have a dodecahedral plane in common, but as she expresses it "the one could only be derived from the other by turning it upside down and rotating through an angle of 60°."

The absence of the common banded structure which customarily denotes twinning in ordinary metallographic preparations does not prove the absence of twinning either in worked or annealed structures. In the former case twinning in very thin lamellae may accompany or even replace slip and pass unrecognized,¹⁸ while in the latter case, instability at twin boundaries may cause obliteration of the banded structure on annealing.

Zinc and Tin

Zinc and tin are strangely alike in the general circumstances of their twinning although unlike in crystal structure. Both metals twin readily when deformed unless the crystals are properly oriented to deform by pure slip, which according to Mark, Polanyi and Schmid takes place primarily along planes of form $\{0001\}$ and secondarily $\{10\bar{1}0\}$ in the case of zinc,¹⁹ and $\{110\}$ or $\{100\}$ in the case of tin.²⁰ The twin bands, whose formation gives rise to the familiar crackling noise known as the tin or zinc cry, have been described in considerable detail by Mathewson and Phillips²¹ in the case of zinc and Edwards²² in the case of tin. Figs. 3 and 4 show the striking similarity of these structures.

The twinning planes in zinc are of the form $\{1012\}$ according to the crystallographic and X-ray measurements on large crystals reported by Mathewson and Phillips and the twin orientation may be duplicated by rotation through 180° around a twinning axis normal to the twinning plane.

¹⁷ C. F. Elam: *Op. Cit.*

¹⁸ Cf. in this connection Rosenhain's reference to Benedicks' views in a discussion of Edwards' paper on Metallic Crystal Twinning. *Jnl. Inst. of Metals* (1915) **14**, 131, and Mügge's observations on translation and twinning in many crystalline substances [*Zeitschr. anorg. Chem.* (1922) **121**, 68].

¹⁹ H. Mark, M. Polanyi and E. Schmid: Vorgänge bei der Dehnung von Zinkkristallen I, II and III. *Zeitschr. Physik.* (1922) **12**, 58.

²⁰ H. Mark, M. Polanyi: Die Gitterstruktur, Gleitrichtungen und Gleitebenen des Weissen Zinns. *Zeitschr. Physik.* (1923) **18**, 75.

²¹ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 143.

²² C. A. Edwards: Metallic Crystal Twinning by Direct Mechanical Strain. *Jnl. Inst. of Metals.* (1915) **14**, 116.

The early evidence that tin twins along planes of form $\{111\}$ and $\{331\}$ has been discussed by Mügge²³ who determined the angles between

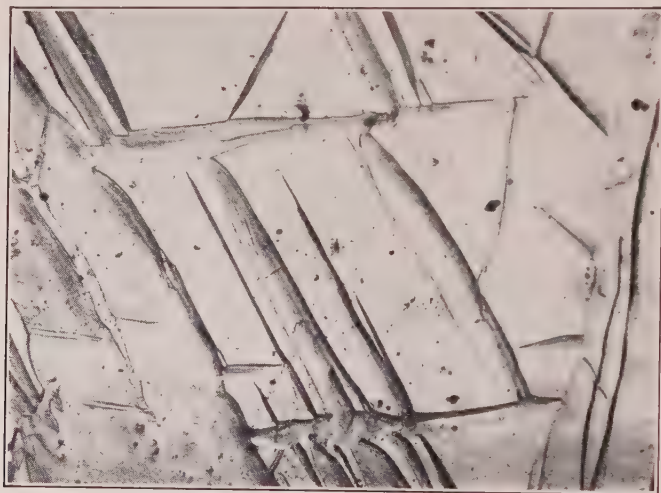


FIG. 3.—TWINS IN ZINC.



FIG. 4.—TWINS IN TIN. (EDWARDS.)

twinning planes in hammered tin crystals and found good agreement with the theoretical requirements for twinning along planes of the latter form in a tetragonal crystal based on the axial ratio 0.3857.

²³ O. Mügge: Über die einfachen Schiebungen am Zinn und seine Zustandsänderung bei 161°. *Zentralbl. für Min.* (1917) 233.

Lead and Nickel

There is ample evidence of abundant twinning in the recorded photomicrographs of the metals lead and nickel in the recrystallized condition. In the case of lead, Humphrey²⁴ has offered evidence of a semi-quantitative character, derived from a study of etching figures, that the straight twin boundaries are parallel to octahedral planes.

Fig. 5, showing many straight boundaries and well defined bands indicative of twinning, is of particular interest as it represents the

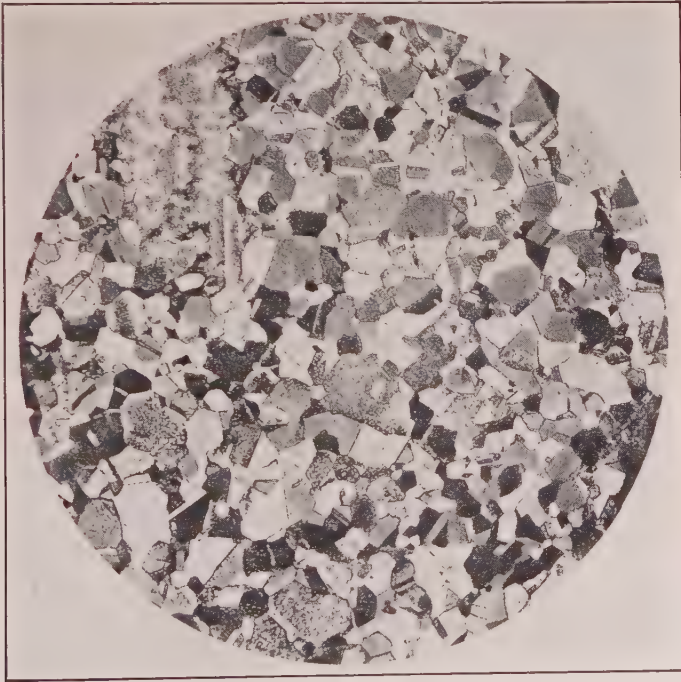


FIG. 5.—TWINS IN SURFACE LAYER OF LEAD CUT WITH A MICROTOME. (F. F. LUCAS.)

recrystallization which occurs spontaneously in the surface layer of lead cut in a microtome and very superficially etched with a solution of hydrogen peroxide and acetic acid. The technique used has been described by F. F. Lucas²⁵ who very kindly prepared this photomicrograph.

GENERAL OCCURRENCE OF TWINNING

If the conditions encountered with the 10 common metals thus far brought into this discussion are fairly representative of metals as a whole,

²⁴ C. W. Humphrey: Effects of Strain on the Crystal Structure of Lead. *Phil. Trans. Roy. Soc.* (1903) **200A**, 225.

²⁵ F. F. Lucas: Application of Microtome Methods to the Preparation of Soft Metals for Microscopic Examination. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 481.

we may express in general terms what Mügge²⁶ has written in regard to iron, namely that twinning (customarily) accompanies the reshaping of a metal (by cold working or cold working and annealing) and that without twinning this change of form would indeed occur in a very different manner.

The Face-centered Cubic Metals

In seeking to classify the phenomena of twinning in the entire list of metals, which for convenience may be grouped according to the various types of crystal structure represented,²⁷ I am struck by the lack of crystallographic data in this field. Thus, I have found no complete description of twinning in any of the six metals, calcium, cerium, cobalt, palladium, rhodium, and thorium, which together with aluminum, copper, gold, iridium, gamma iron, lead, nickel, platinum and silver, constitute the face-centered cubic group.

A summary of the incomplete information now available is given in Table 1.

TABLE 1.—*Face-centered Cubic Metals*

Metal	Twinning	Composition Plane	Twinning Axis
Aluminum.....	Questionable		
Calcium.....			
Cerium.....	Probable		
Cobalt.....	Probable		
Copper.....	Clearly defined	{111}	[111]
Gold.....	Clearly defined	{111}	[111]
Iridium.....	Clearly defined	{111}	[111]
Gamma iron.....	Clearly defined	{111}	[111]
Lead.....	Clearly defined	{111}	[111]
Nickel.....	Good microscopic evidence		
Palladium.....			
Platinum.....	Clearly defined	{111}	[111]
Rhodium.....			
Silver.....	Clearly defined	{111}	[111]
Thorium.....			

In the case of cerium, the banded structure found by Schumacher and Lucas²⁸ in samples of pure metal may be accepted as qualitative evidence of twinning. This is illustrated in Fig. 6.

²⁶ *Zeitschr. anorg. Chem.* (1922) **121**, 68.

²⁷ *International Critical Tables* (1926) **1**, 338.

²⁸ E. E. Schumacher and F. F. Lucas: Photomicrographic Evidence of the Crystal Structure of Pure Cerium. *Jnl. Amer. Chem. Soc.* (1924) **46**, 1167.



FIG. 6.—BANDED STRUCTURE IN PURE CERIUM. (F. F. LUCAS AND E. E. SCHUMACHER.)

Vogel²⁹ has drawn attention to striae believed to be deformational twins found in the surface layers of cobalt, nickel and various alloys after grinding and polishing. So-called annealing twins are familiar elements in the microstructure of nickel and its alloys such as invar, nichrome, permalloy and monel metal, but I do not find that any precise crystallographic study of these twin bands has ever been undertaken.

The Body-centered Cubic Metals

No precise record of twinning has been found in the case of any of the body-centered metals, which, together with alpha iron, are listed in Table 2.

TABLE 2.—*Body-centered Cubic Metals*

Metal	Twinning	Twinning Plane	Twinning Axis
Chromium.....	Not observed		
Alpha iron.....	Clearly defined	{112}	[111]
Lithium.....			
Molybdenum.....	Not observed		
Potassium.....			
Sodium.....			
Tantalum.....			
Tungsten.....	Not observed		
Vanadium.....	Recorded by Groth ^a	{443}?	[443]?

^a P. H. Groth: *Chem. Kristall.* The original paper by Setterberg is inaccessible.

It is rather generally believed that body-centered cubic metals do not form twin crystals. To maintain this point of view it should be necessary to prove that Neumanns in alpha iron are not twin lamellae and that the twins so fully described by McKeehan are merely pseudomorphs of twins originally formed in austenite at a higher temperature. The latter situation would imply that when gamma iron changes to alpha iron certain twin boundary planes of form {111} in the face-centered lattice become converted perhaps without any change of position into composition planes of form {211} between the new crystal and new twin in the body-centered lattice. In order to account fully for the boundary conditions observed in these alpha twins it would be necessary to assume that some other part of an original gamma twin boundary moves into the position of a second boundary plane of form {211} between the same alpha twin and the rest of the crystal.

G. Edmunds at the Hammond Laboratory has been unable to find twin lamellae in the fragments produced by hammering samples of chromium, molybdenum, tantalum, tungsten and vanadium.

²⁹ R. Vogel: Über Zwillingsbildung in den Oberflächen Schichten von Metallen infolge Kaltbearbeitung. *Zeitschr. anorg. Chem.* (1921) **117**, 271.

Nothing is known concerning the behavior of the alkali metals in respect to twinning.

The Hexagonal Metals

The metals allied to zinc, except mercury, in the hexagonal close-packed group have been studied by Mathewson and Phillips,³⁰ who find twinning on planes of form $\{10\bar{1}2\}$ in every case quite in conformity with the twinning behavior of zinc (see Table 3). No other metal in this group has been studied from the present point of view.

TABLE 3.—*Hexagonal Close-packed Metals*

Metal	Twinning	Twinning Plane	Twinning Axis	Axial Ratio
Beryllium.....	Clearly defined	$\{10\bar{1}2\}$	$[1012]$	1.58
Cadmium.....	Clearly defined	$\{10\bar{1}2\}$	$[10\bar{1}2]$	1.89
Cerium.....				1.62
Cobalt.....				1.633
Hafnium.....				1.64
Magnesium.....	Clearly defined	$\{10\bar{1}2\}$	$[10\bar{1}2]$	1.624
Osmium.....				1.59
Ruthenium.....				1.59
Titanium.....				1.59
Zinc.....	Clearly defined	$\{10\bar{1}2\}$	$[10\bar{1}2]$	1.86
Zirconium.....				1.59

Other Metals of Known Crystal Structure

The remaining metals of known crystal structure are grouped in Table 4. Twinning in antimony and bismuth by pressure was described

TABLE 4.—*Miscellaneous Metals*

Metal	Twinning	Twinning Plane	Twinning Axis	Form of Lattice
Antimony.....	Clearly defined	$\{01\bar{1}2\}^a$	$[01\bar{1}2]$	Hex.-rhombohedral
Bismuth.....	Clearly defined	$\{01\bar{1}2\}^a$	$[01\bar{1}2]$	Hex.-rhombohedral
Germanium.....				Diamond cubic
Indium.....	Microscopic evidence	b		Face-centered tetragonal
Tellurium.....				Hex.-rhombohedral
Tin (gray).....				Diamond cubic
Tin (white).....	Clearly defined	$\{331\}$ or $\{111\}?$	$[331]$ or $[111]?$	Tetragonal of special form

^a See Footnote 31.

^b See Footnote 32.

³⁰ C. H. Mathewson and A. J. Phillips: Twinning in Beryllium, Magnesium, Zinc, and Cadmium. See p. 445.

by Mügge more than 40 years ago.³¹ Carpenter and Tamura³² have photographed twin bands of the usual appearance in a deformed and annealed sample of indium. Germanium and tellurium remain untouched in this field of investigation.

Metals of Unknown Crystal Structure

I have found no record of twinning either qualitative or quantitative in any of the remaining metals: actinium, columbium, gallium, manganese, mercury, niobium, polonium, radium, scandium, thallium, uranium, yttrium and rare earth metals.

Summary

It may be said in concluding this survey that twinning in one form or another is an ordinary feature of the microstructure of all the familiar metals except aluminum. It is known to occur in some of the other metals but comparatively few have been investigated. Obviously the absence of twinning cannot be postulated in any of the negative cases. For example, it has not been demonstrated, although it may appear improbable, that twinning has no part in the fragmentation and fibering of tungsten by swaging, as described by Smithells.³³

Twinning therefore is prevalent in metals and consequently a factor of great influence on the shape, size, and particularly the orientation of the crystalline particles formed when metals are forced to change their shape by mechanical treatment and brought to various temper conditions by annealing.

SOME OBSERVATIONS ON TWINNING AND RECRYSTALLIZATION IN WROUGHT METALS OF THE HEXAGONAL AND CUBIC GROUPS

This includes most of the metals. The experimental work is restricted to one metal in each group. Only in the case of zinc are the observations systematic from a crystallographic point of view and even in this case the work is incomplete in many directions. Iron is discussed quite briefly on the basis of Krivobok's experiments.³⁴ The observations on copper are for the most part fragmentary and circumstantial. Nevertheless, there is a continuity of circumstance and an undercurrent of analogy pointing to a general group of postulates or provisional assertions, which may at least stir up an amount of useful discussion.

³¹ O. Mügge. Über künstliche Zwillingsbildung durch Druck am Antimon, Wis-muth und Diopsid. *Neue Jahrb. für Min.* (1886) **1**, 183.

³² H. C. H. Carpenter and S. Tamura: The Formation of Twinned Metallic Crystals. *Proc. Roy. Soc.* (1926-27) **113A**, 161.

³³ C. J. Smithells: Tungsten. 1926. Chapman & Hall, London.

³⁴ V. N. Krivobok: A Photomicrographic Study of the Process of Recrystallization in Certain Cold-worked Metals. A. I. M. E. Pamphlet No. 1557-E (1926).

Rolled Zinc

With adaptable single crystals at hand, it appears to be a simple matter to plan and execute a set of experiments in which various selected orientations are deformed plastically by rolling, and critically examined under the microscope from time to time as they change structurally during the process.

In practice, difficulties were found which have thus far limited the work to the rolling of thin sections bounded top and bottom by basal cleavages. Chilled flat-metal single crystals about $\frac{1}{4}$ in. thick with their basal planes nearly perpendicular to the surface could be broken quite easily along these planes by simply bending or forcing a sharp blade into the metal in the desired region. In this way sections down to 1 mm. thick were produced without twinning except in a few localized areas.

In any small-scale laboratory study of a rolling process the advantage of having a specimen with two perfectly flat and parallel surfaces cannot be overestimated. It is, of course, impossible to retain this advantage

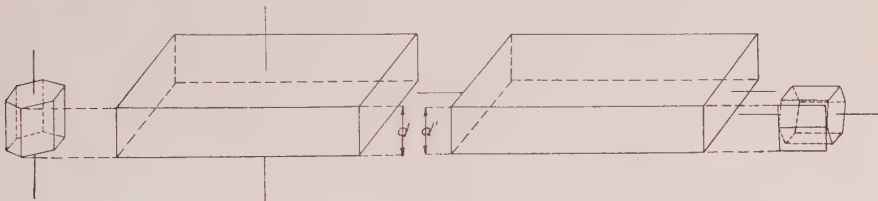


FIG. 7.—APPROXIMATE CHANGE IN ORIENTATION DUE TO SIMPLE TWINNING IN ZINC.

in specimens of other orientations, which must be cut to specifications from the original single crystal. The operations of cutting, grinding and polishing such small samples, even when conducted with extreme care, produce an amount of twinning which materially changes the reaction of the material to rolling or other designated forms of stress.

A great many experiments were made with cleavage sections of different thickness rolled various amounts either continuously or in stages.

Only the most general conclusions will be presented here, together with such illustrations as seem necessary to give them force and clarity.

If we imagine the atoms in a basal cleavage section of thickness d to be completely rearranged by twinning along one set of planes of form $\{10\bar{1}2\}$ without changing the horizontal plane of the section, the vertical hexagonal axis assumes a position only 4° removed from the horizontal and the thickness decreases 7.21 per cent.

This is nearly equivalent to turning the unit hexagonal prism on its side as shown in Fig. 7 so that the thickness which was originally proportional to the height ($d = 1.862$) becomes nearly proportional to the distance between prismatic faces ($d' = \sqrt{3}$).

If the twinning occurs in different parts of the specimen along different planes of form $\{10\bar{1}2\}$ —for example, $(01\bar{1}2)$, $(0\bar{1}12)$, $(1\bar{1}02)$, and $(\bar{1}102)$ —the hexagonal axis will assume different directions, 60° apart, in planes 4° from the horizontal and the reduction in thickness may be somewhat less than in the simple case owing to redistribution of the strain which is theoretically in evidence at twin boundaries when we follow a simple geometrical plan of bringing the atoms up to a common composition plane.

With large portions of the specimen dominated by a single set of twinning planes this effect would of course be negligible, but with an involved interlacing of minute twins it might be considerable.

The conditions observed by K. R. Van Horn in the Hammond Laboratory experiments favor the simple interpretation. Many basal cleavage sections rolled to a reduction of 6 to 7 per cent. contained

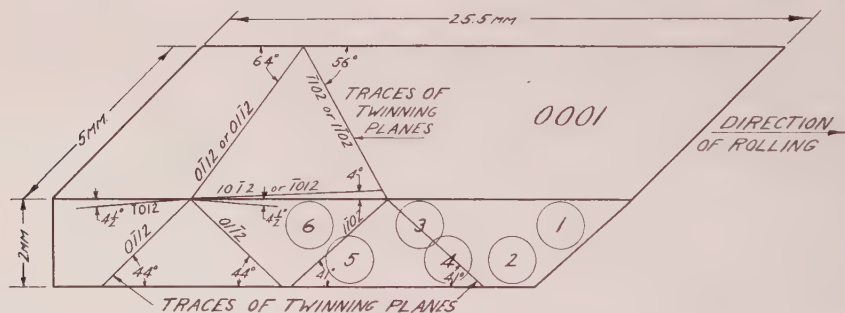


FIG. 8.—POSSIBLE TWINNING PLANES AND SPOTS PHOTOGRAPHED IN A ROLLED BASAL CLEAVAGE SECTION OF A ZINC CRYSTAL.

large regions wholly converted to a single preferred twin orientation. The prevailing conditions are represented by the following analysis of one specimen. The dimensions and orientation of this specimen are shown in Fig. 8.

The thickness was reduced 6.98 per cent. by two passes through a small set of hand-operated rolls. The specimen was then dipped in moderately concentrated nitric acid and examined on both rolled surfaces under the microscope. In this work plane, polarized light was passed

FIG. 9.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. TOP SURFACE IN FIG. 8.

FIG. 10.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. TOP SURFACE IN FIG. 8.

FIG. 11.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. BOTTOM SURFACE IN FIG. 8.

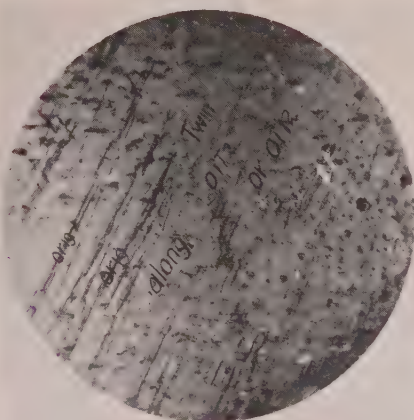
FIG. 12.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. BOTTOM SURFACE IN FIG. 8.

FIG. 13.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (1) IN FIG. 8.

FIG. 14.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (2) IN FIG. 8.

(Reduced to $\frac{3}{4}$ original scale, original magnification given.)

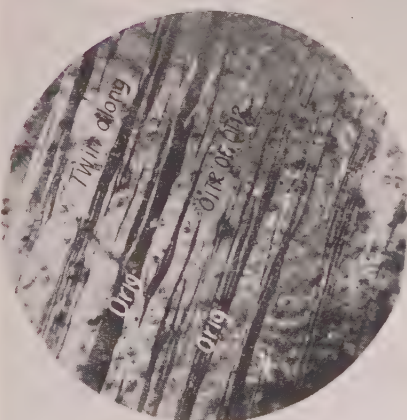
9



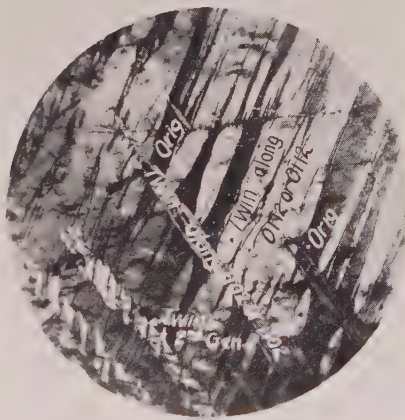
10



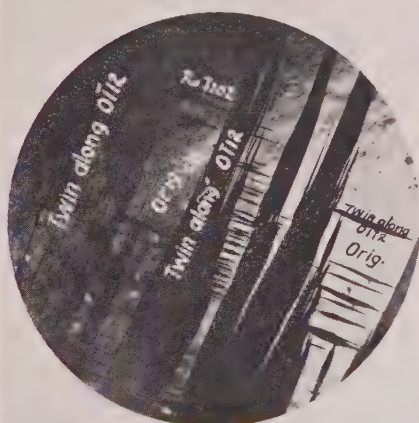
11



12



13



14



through a vertical illuminator and, after reflection from the surface of the specimen, through an analyzing nicol prism which was usually set to extinguish light vibrating in the original (non-rotated) plane of

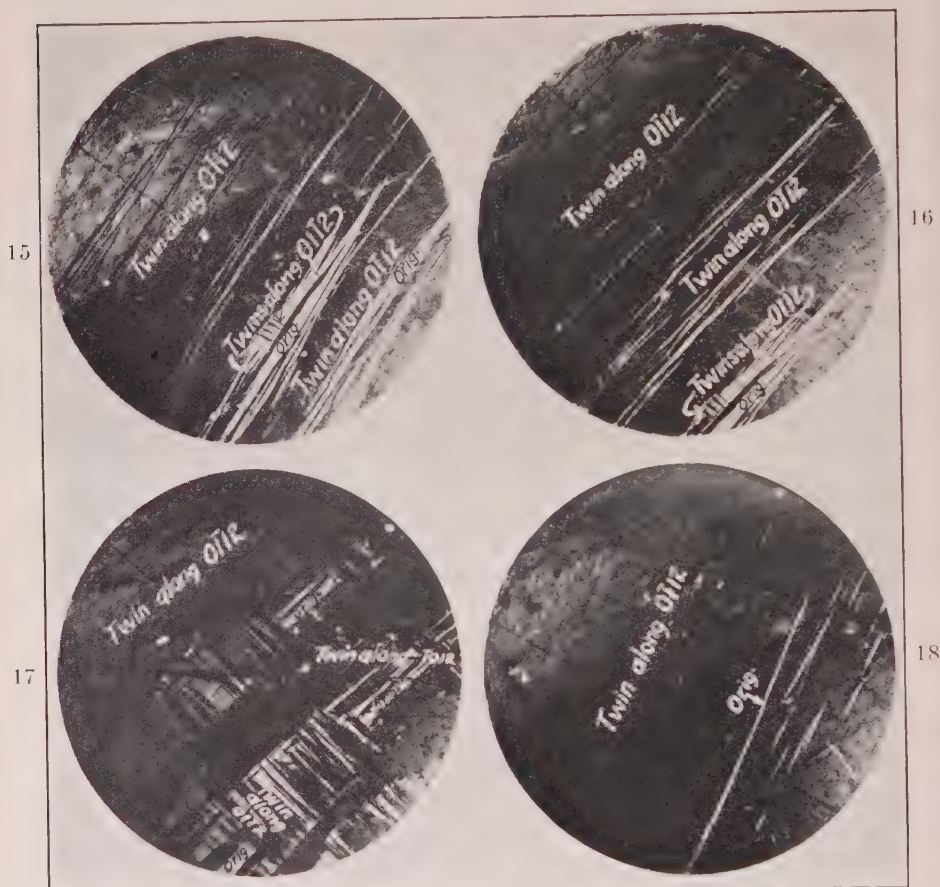


FIG. 15.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (3) IN FIG. 8.

FIG. 16.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (4) IN FIG. 8.

FIG. 17.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (5) IN FIG. 8.

FIG. 18.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. STRUCTURE AT (6) IN FIG. 8.

(Reduced to $\frac{3}{4}$ original scale, original magnification given.)

polarization. On rotating the stage, contrast could be developed between the various structure elements and twin bands could be identified either by measuring the angles between various twinning planes or determining the positions of complete parallel extinction. For quantitative work the former method was preferred as it was less influenced by surface

inequalities due to variable etching, wavy rolling, etc. Unaltered basal surfaces which normally should be optically isotropic actually remained uniformly dark during complete rotation through 360° .

Figs. 9, 10, 11, and 12 represent several portions of the top and bottom surfaces photographed between crossed nicols and marked for identification of the structure elements shown. In all of these photos only small remnants of the original base $\{0001\}$ are visible. *Almost the entire substance of the crystal has been transformed by twinning into another crystal.* Bands or patches formed by twinning along all possible planes of form $\{10\bar{1}2\}$, six in number, are combined in the new crystal. The distribution varies in different parts of the crystal but it can be stated that $(0\bar{1}12)$ and $(01\bar{1}2)$ are strongly preferred planes of twinning in this specimen while $(10\bar{1}2)$ and $(\bar{1}012)$ merely contributed a few bands along the edge due to bending stresses set up when the original cleavages were made.³⁵

Figs. 9 and 10 show that either $(0\bar{1}12)$ or $(01\bar{1}2)$ are preferred planes at the top of the specimen and Figs. 11 and 12 that a similar condition exists at the bottom surface. These planes come nearest into line with the axis of revolution of the rolls.

The nature of this preference is revealed by examining the sides, which had to be smoothed and polished carefully with fine abrasive to remove the roughness due to rolling and at the same time retain the original structure. The beveled end, which was a natural feature of the specimen, entered the rolls first, as shown in Fig. 8. At the spot marked 1, about halfway down the beveled edge, less than half of the metal (shown white in Fig. 13) retains its original orientation and the rest (shown dark in Fig. 13) is twinned in general along the $(0\bar{1}12)$ planes. A few narrow bands twinned along $(01\bar{1}2)$ planes may be seen at the right and in the upper center a band twinned along $(\bar{1}102)$.

At the spot marked 2, just beyond the beveled edge, represented by Fig. 14, very little of the original crystal remains and the metal is principally composed of twins along $(0\bar{1}12)$ coming down from the top and $(01\bar{1}2)$ coming up from the bottom.

This condition is typical of the structure at other locations with the added qualification that the two varieties of preferred twins occur in variable quantities with the first always in excess. Thus Fig. 15, representing the spot marked 3 near the top of the specimen, shows only traces of the second preferred twin; Fig. 16, a spot (4) near the bottom, about the same; Fig. 17, another spot (5) near the bottom, considerably more of the second twin and finally Fig. 18, a spot near the upper center,

³⁵ The identity of these bands is fixed by tracing them across the edge into the upper or lower surface. It may be noted that the pair $(0\bar{1}12)$ and $(01\bar{1}2)$ can easily be distinguished from the pair $(\bar{1}102)$ and $(1\bar{1}02)$ on the surface and the pair $(0\bar{1}12)$ and $(1\bar{1}02)$ from the pair $(01\bar{1}2)$ and $(\bar{1}102)$ on the edge.

virtually a complete transformation by twinning along $(0\bar{1}12)$ planes. The last figure also represents the structure of the rest of the material visible on this section.

The opposite side of the specimen shows a more general participation of the other two twinning planes $(1\bar{1}02)$ and $(\bar{1}102)$. Various conditions of preferred twinning along the four predominant planes are observed on examination of different cleavage specimens from the same crystal. When the direction of rolling is exactly parallel to the edge, the planes $(0\bar{1}12)$ and $(01\bar{1}2)$ are inclined 26° and the planes $(1\bar{1}02)$ and $(\bar{1}102)$ 34° to the axis of revolution of the rolls. Thus an inconsiderable displacement of 4° in the right direction as the specimen passes

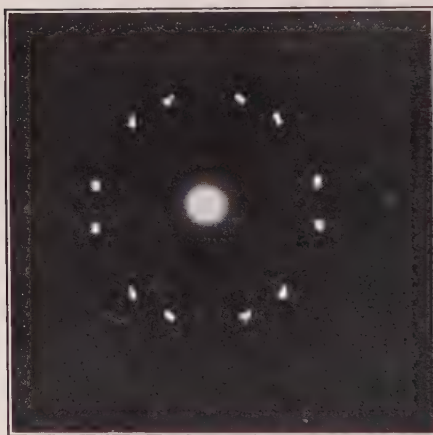


FIG. 19.—LAUE PATTERN FROM UNTWINNED BASAL CLEAVAGE.

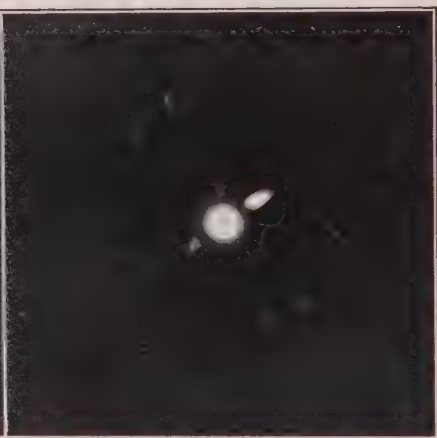


FIG. 20.—LAUE PATTERN FROM BASAL CLEAVAGE REDUCED 6 TO 7 PER CENT. IN THICKNESS BY COLD ROLLING.

through the rolls should bring these two sets of planes into equivalent action.

This condition was actually discovered by R. M. Bozorth of the Bell Telephone Laboratories in a Laue pattern³⁶ of one of these specimens which had been reduced 6.6 per cent. in thickness by one pass through the rolls. Another specimen rolled almost exactly the same amount furnished a pattern showing one predominant twin. The pattern from an untwinned cleavage is shown in Fig. 19 and one of the altered patterns in Fig. 20. So much of the radiation was absorbed by these specimens, which were about $1\frac{1}{2}$ mm. thick, that only the most strongly reflecting planes are recorded in the halftones. These are the planes of form $\{12\bar{3}1\}$ in the original crystal responsible for twelve spots equidistant from the center and basal planes from four twins inclined 86° to the

³⁶ General radiation from a tungsten target was employed in this and similar experiments and the beam was directed at right angles to the cleavage surface.

cleavage surface represented by one bright spot and three much fainter spots of varying intensity near the center.

It is observed that the spots from the original crystal are scarcely discernible in Fig. 20 while the dominant intensity of the spot just above and to the right of the spot formed by the undeviated beam indicates that the crystal is principally composed of material twinned along the preferred plane (0112). The original negative also revealed faint spots which could be referred to planes of form (2130) and (2131) in the twin. The elongated and generally ragged appearance of all diffraction spots from rolled samples is attributed to distortion associated

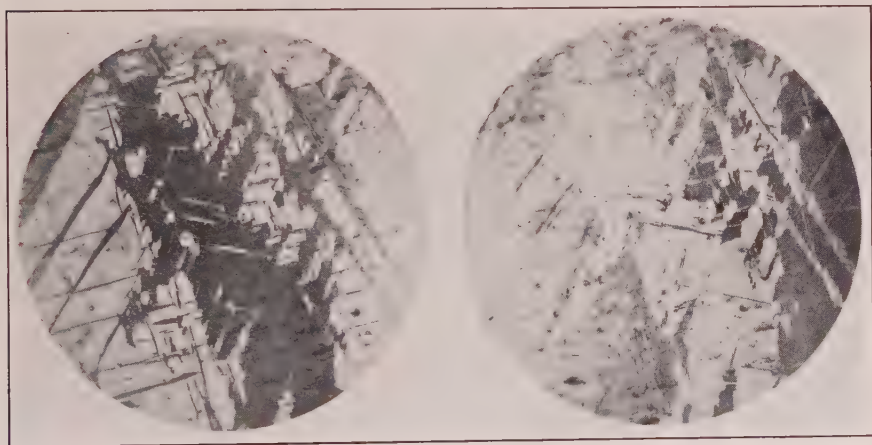


FIG. 21.

FIG. 22.

FIG. 21.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. BASAL CLEAVAGE SECTION REDUCED 18 TO 19 PER CENT. IN THICKNESS BY COLD ROLLING. REACTION BETWEEN TWIN BANDS (0112) AND (1102) THE LATTER ROTATED TO A POSITION OF EXTINCTION. NARROW INTERNAL TWIN BANDS OF SECOND GENERATION VISIBLE.

FIG. 22.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. BASAL CLEAVAGE SECTION REDUCED 18 TO 19 PER CENT. IN THICKNESS BY COLD ROLLING. REACTION BETWEEN TWIN BANDS (0112) AND (1102) THE FORMER ROTATED TO A POSITION OF EXTINCTION. NARROW TWIN BANDS OF SECOND GENERATION VISIBLE.

(Reduced to $\frac{3}{4}$ original scale, original magnification given.)

with the twinning and the accompanying basal slip revealed by slip bands in some of the twinned portions along an edge which had been carefully polished and lightly etched before rolling.

When these cleavage sections are rolled beyond the amount required for complete twinning, further extension must take place by some slipping process. Planes of the two forms representing the closest atomic packing, viz., {0001} nearly vertical and {10 $\bar{1}$ 0} nearly horizontal, seem to be unfavorably located for slip, but the polished and etched side of the specimen described in Fig. 8 showed numerous faint striae parallel to both of these planes when it was rolled to a further slight reduction. In addition some of the twin bands along the principal

preferred plane ($0\bar{1}12$) contained striae inclined about 67° to the edge, not greatly different from the value 64° which would represent the traces of twinning planes yielding certain twins of a second generation actually observed in the primary bands (*d* in Fig. 25). In some places curved striae were observed. It is concluded that there is a complication of slip and twinning along several sets of planes accompanied by a certain amount of distortion.

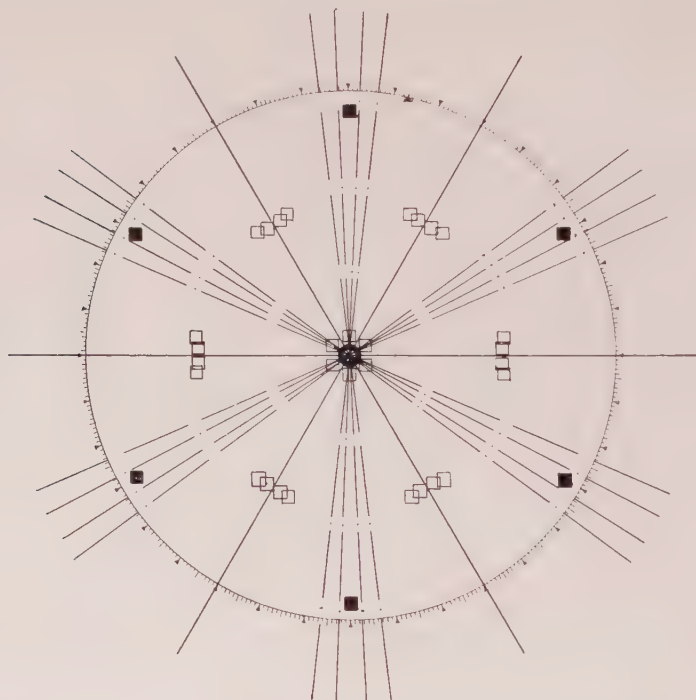


FIG. 23.—STEREOGRAPHIC PROJECTION OF BASAL PLANES IN A ZINC CRYSTAL AND ALL POSSIBLE TWINS THROUGH TWO GENERATIONS, SHOWING TRACES OF THESE PLANES IN THE PLANE OF THE PROJECTION.

- = pole of basal plane in the original crystal.
- = poles of basal planes in twins of the first generation.
- = poles of basal planes in twins of the second generation.

The surface structure of a specimen reduced 18.9 per cent. in thickness in three passes through the rolls furnishes considerable evidence concerning the nature of recrystallization. The customary angular intergrowths of twin bands sometimes including lamellae of the original crystal develop by interchange of material across the boundaries into more or less rounded dendritic forms, with the frequent occurrence of detached lobes or branches. This effect, which is illustrated in Figs. 21 and 22, taken between crossed nicols, represents recrystallization in the limited sense that there has been a granulation and redistribution but not a

pronounced reorientation of the material. It is commonly regarded as spontaneous recrystallization during working in conformity with the well known fact that cold-rolling of zinc substantially at room temperature produces the type of alteration which is usually associated with the hot-working of metals. In taking Fig. 21, the stage was rotated to bring the central dendritic patch with its appendages into a position of complete extinction. A simple analysis with the aid of a stereographic projection of the basal planes in the crystal and all possible twins through two generations, shown in Fig. 23, identifies this patch as an original (preferred) twin along $(1\bar{1}02)$ planes; *viz.*, a line perpendicular to a line joining the pole of a basal plane, as reorientated by twinning, with the

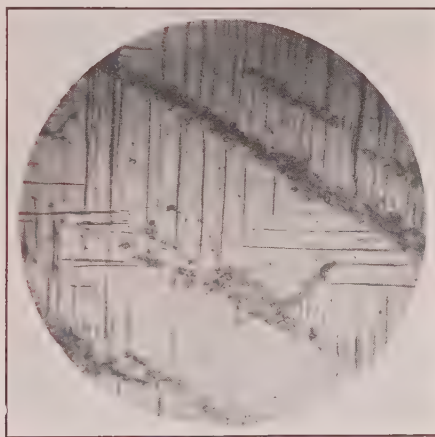


FIG. 24.—ZINC IN POLARIZED LIGHT. CROSSED NICOLS. $\times 100$. BASAL CLEAVAGE SECTION REDUCED 18 TO 19 PER CENT. IN THICKNESS BY COLD ROLLING. TWIN BANDS OF THE SECOND GENERATION INTERSECTING AT 88° IN AN ORIGINAL TWIN ALONG $(0\bar{1}12)$ PLANES VIEWED IN THE CLEAVAGE SURFACE.
(Reduced to $\frac{3}{4}$ original scale, original magnification given.)

center of the projection gives one of the four positions of extinction when this twin is rotated in the plane of the original basal cleavage. Fig. 22 represents the same location on the specimen rotated to produce extinction of the conspicuous intergrowth. This proves to be a twin parallel to $(0\bar{1}12)$ planes.

Complex twinning was expected in the hard-rolled specimens and in the present case is particularly well represented by two varieties of twins belonging to a second generation derived from original twin bands along $(0\bar{1}12)$ planes. These intersect approximately at right angles as shown in Fig. 24 and the poles of their corresponding twinning planes are located at *a* and *b* in Fig. 25, which is a projection in the original cleavage plane of the poles of all possible twinning planes through two generations. The lines *a'* and *b'* represent the traces of these planes in the original base and the angle between them is 88° . The poles representing other twins

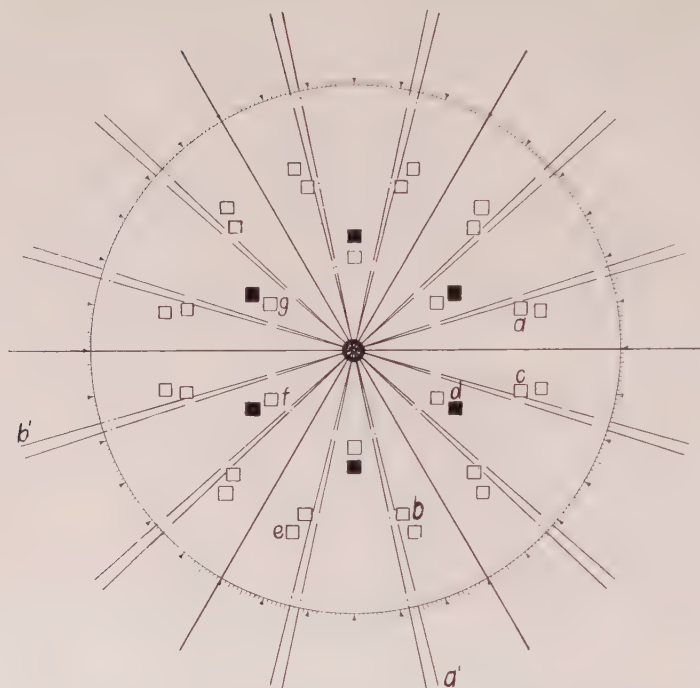


FIG. 25.—STEREOGRAPHIC PROJECTION OF TWINNING PLANES IN A ZINC CRYSTAL AND ALL POSSIBLE TWINS THROUGH TWO GENERATIONS, SHOWING TRACES OF THESE PLANES IN THE ORIGINAL BASAL PLANE, WHICH IS THE PLANE OF THE PROJECTION.

- = pole of basal plane in the original crystal.
- = poles of twinning planes yielding twins of the first generation.
- = poles of twinning planes yielding twins of the second generation.

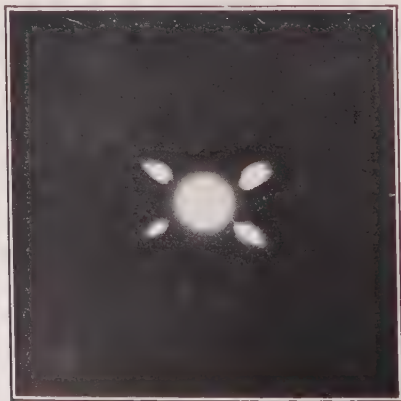


FIG. 26.—LAUE PATTERN OF BASAL CLEAVAGE SECTION REDUCED 18 TO 19 PER CENT. IN THICKNESS BY COLD ROLLING.

belonging to a second generation observed in this specimen are marked *c*, *d*, *e*, *f*, and *g* in Fig. 25.

The Laue pattern obtained from this specimen is given in Fig. 26. An outer grouping of faint spots (not visible in the reproduction) corresponding to the prominent spots in Fig. 19 proves that some of the

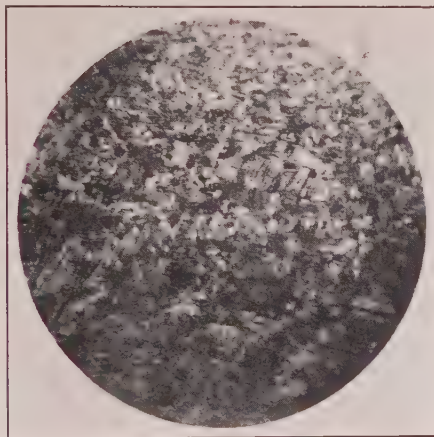


FIG. 27.—ZINC IN POLARIZED LIGHT. BASAL CLEAVAGE SECTION REDUCED 50 PER CENT. IN THICKNESS BY COLD ROLLING. RECRYSTALLIZATION WITH DIVERSITY OF ORIENTATION.

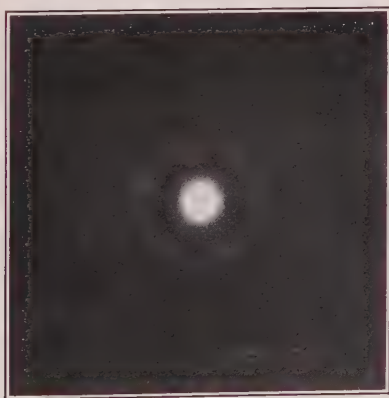


FIG. 28.—LAUE PATTERN OF BASAL CLEAVAGE SECTION REDUCED 50 PER CENT. IN THICKNESS BY COLD ROLLING.

original crystal still remains. This may indicate that a concentration of impurities in certain parts of the crystal has prevented the atomic movements required for twinning. An interesting discussion of effects of this character as related to pure slip has been contributed this year by M. J. Buerger.³⁷ The extreme faintness of spots at the extremities of a

³⁷ M. J. Buerger: The Cause of Translation Striae and Translation Strain-hardening in Crystals. See p. 375.

vertical diameter through the central group indicates that practically no twins had developed along (1012) and $(\bar{1}012)$ planes in the cubic millimeter of material traversed by the X-ray beam. The prominence of the other four spots signifies that the specimen is for the most part

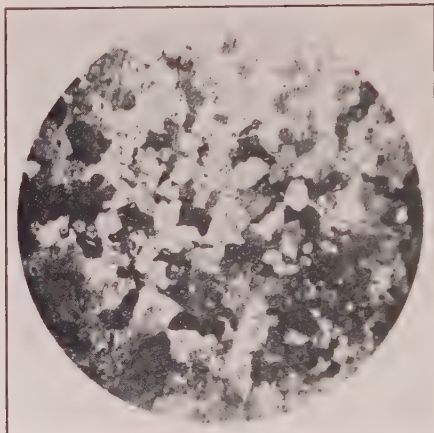


FIG. 29.—ZINC IN POLARIZED LIGHT. BASAL CLEAVAGE SECTION REDUCED 50 PER CENT. BY COLD ROLLING AND ANNEALED 10 MIN. AT 250°C . RECRYSTALLIZATION AND GRAIN GROWTH.

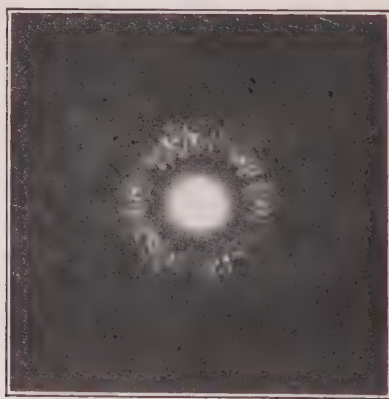


FIG. 30.—LAUE PATTERN OF BASAL CLEAVAGE. SECTION REDUCED 50 PER CENT IN THICKNESS BY COLD ROLLING AND ANNEALED 10 MIN. AT 250°C .

composed of twins formed along the four planes, $(0\bar{1}12)$, $(01\bar{1}2)$, $(1\bar{1}02)$, and $(\bar{1}102)$.

Part of the etched surface of a specimen reduced 50 per cent. in thickness by cold rolling is shown in Fig. 27. It is probable that the prevailing fine granulation is a result of reaction between descendent twin lamellae just as the coarse granulation in an earlier stage came from the original

twins. This might result in a sufficient diversity of orientation to account for the Laue pattern which is reproduced in Fig. 28. The original crystal seems to have disappeared but the positions of the six original twins are marked by selective groupings of the diffraction spots in the central ring. These details are unsatisfactory in the reproduction.

A piece of this specimen was annealed for ten minutes at 250° C. The microstructure given in Fig. 29 and the Laue pattern in Fig. 30 reveal grain growth but at present it is not possible to decide whether any new orientations have been produced, apart from those which would approximate the requirements of complex twinning. It may be stated that a full complement of twins through only three generations would permit no angle greater than 5° to separate adjacent traces of planes of form {0001} in the original cleavage surface.

Hammered Iron and Rolled Beta Brass

Krivobok's experiments³⁸ demonstrate that the recrystallization effected by annealing pure electrolytic iron or iron containing about 1.75

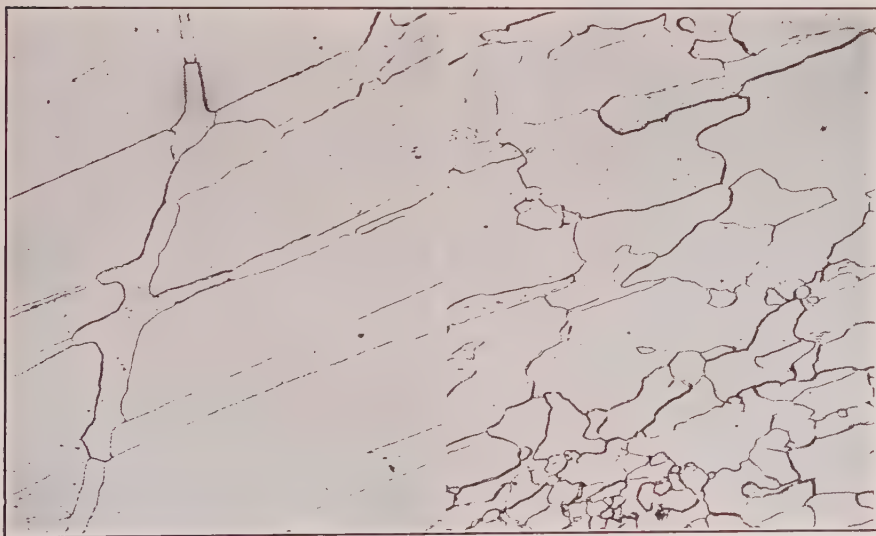


FIG. 31.—AN EARLY STAGE OF RECRYSTALLIZATION IN SILICON-FERRITE PRODUCED BY ANNEALING AFTER COLD-HAMMERING. (KRIVOBOK.)

FIG. 32.—A LATER STAGE OF RECRYSTALLIZATION IN SILICON-FERRITE. (KRIVOBOK.)

per cent. of silicon, previously reduced 25 per cent. in thickness by cold hammering, can be definitely traced to numerous Neumann bands which he regarded as the principal seat of strain in the cold-worked material, without attempting to define their constitution. An assumption that they are mechanical twins with distortion at the boundaries would favor

³⁸ V. N. Krivobok: *Op. cit.*

the deductions drawn from these experiments. Two of the many excellent photographs included in the paper are reproduced for the purpose of illustrating some of the significant transformations observed.

In Fig. 31 a band near the left-hand margin has developed into a dendritic growth by invading the original crystal on both sides and feeding along several intersecting bands. The similarity between this process and the reaction between twin bands in zinc is quite evident. In the present case the original bands are narrow intrusions in a predominant volume of the original crystal and nothing is known concerning the orientations of the various components either before or after the transformation. That the entire substance of the crystal may be irregularly partitioned by growth emanating from these narrow bands is evident on inspection of Fig. 32 in which the directional influence of the bands can be seen in spite of their partial disintegration and subsequent growth in various directions.

There has been a general failure to recognize any participation of twinning in the general process of deformation and recrystallization as observed in iron of the usual fine-grained structure. Chappell,³⁹ who carefully studied recrystallization in iron wire containing 0.07 per cent. carbon, in describing the first stage writes as follows: "These granular markings (representing the first change on annealing), indicating disintegration and incipient recrystallization of the deformed ferrite crystals, very often take the form of roughly parallel and curved bands crossing the crystals obliquely to the longitudinal axis."

How much of this failure may be attributed to the extremely minute size of the strain markings and the first elements of recrystallization, making it difficult to recognize any eventual participation of twins in the process and how much to the alleged circumstance that Neumann bands are produced only by special forms of deformation cannot be predicted. It is perhaps significant that these special conditions, namely, shock in coarse-grained metal, would particularly favor the production of twin bands large enough to be recognized without difficulty. So keen an observer as L. W. McKeehan⁴⁰ has suggested, as an alternative to the columnar slipping proposed by Taylor and Elam⁴¹ to account for curved slip bands in iron, twinning on a very fine scale with zigzag boundaries which would be possible on account of the peculiar relation of twins along planes of form $\{211\}$ in a body-centered cubic structure.

Good photomicrographs illustrating mechanical twinning in rolled beta brass may be found in Miss Clark's paper on heat treatment of 60-

³⁹ C. Chappell: The Recrystallization of Deformed Iron. *Jnl. Iron and Steel Inst.* (1914) **89**, 460.

⁴⁰ L. W. McKeehan: *Op. cit.*

⁴¹ G. I. Taylor and C. F. Elam: The Distortion of Iron Crystals. *Proc. Roy. Soc.* (1926) **112A**, 337.

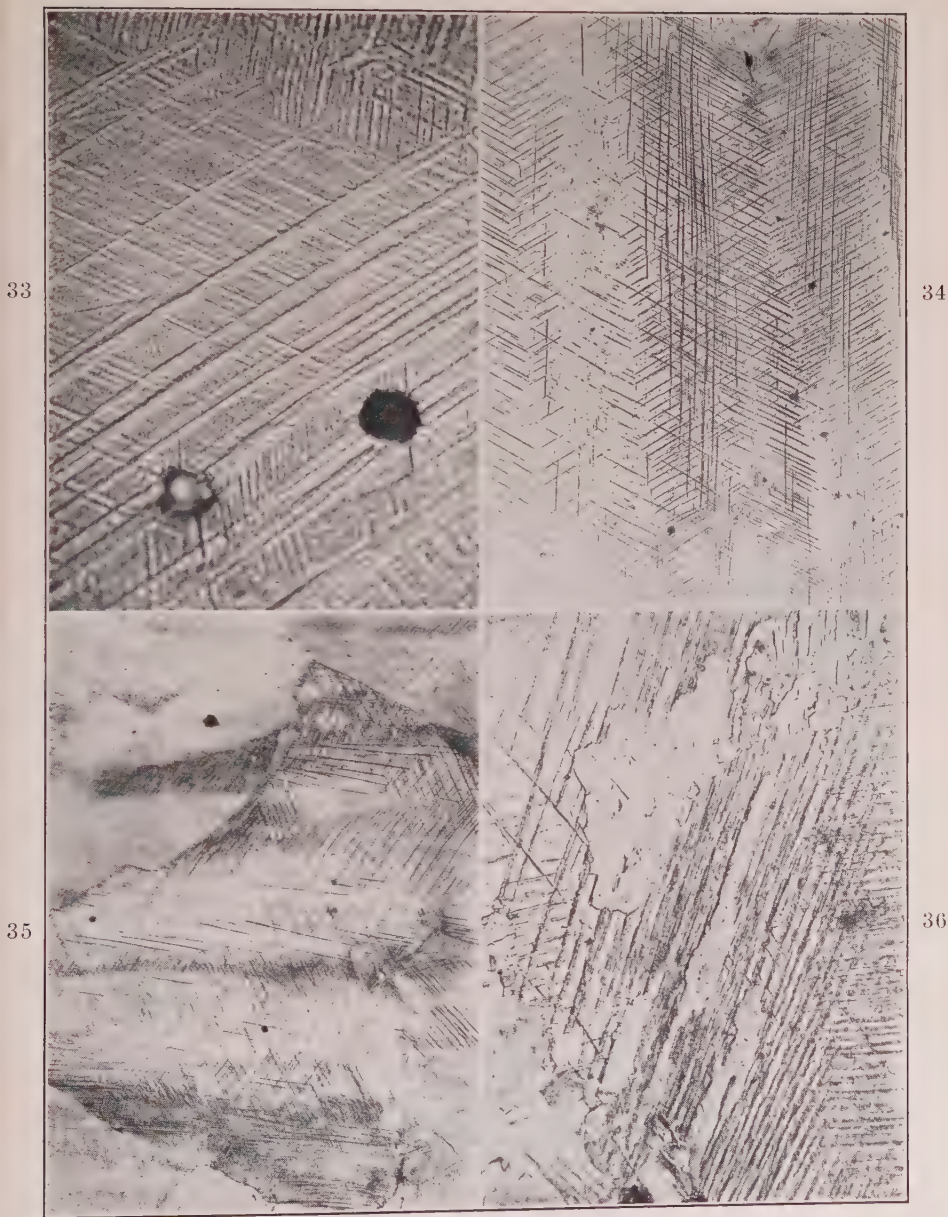


FIG. 33.—DEFORMATIONAL STRIAE IN TIN BRONZE. $\times 1000$.

FIG. 34.—DEFORMATIONAL STRIAE IN A SINGLE CRYSTAL OF ALPHA BRASS. $\times 100$.

FIG. 35.—DEFORMATIONAL STRIAE IN ALPHA BRASS. $\times 75$.

FIG. 36.—A VERY EARLY STAGE OF RECRYSTALLIZATION IN ALPHA BRASS. $\times 500$.

(Reduced to $\frac{4}{5}$ original scale, original magnification given.)

40 brass.⁴² In a discussion of that paper⁴³ I pointed out the intimate connection between twinning and recrystallization observed in a pure beta brass with about 53 per cent. of copper. There are many points of similarity in the recrystallization of alpha iron and beta brass and it is noteworthy that both possess the body-centered cubic type of structure.⁴⁴

Copper and Its Alpha Solutions

Bands of detectable width at once suggesting twin lamellae are not infrequently observed in microsections of strained copper, brasses and bronzes. As in the other examples of mechanical twinning, deformation by impact is especially productive of these markings, which belong to the group designated Non-effaceable Deformation Figures by Osmond and Cartaud,⁴⁵ and correspond to the ones found by these authors in face-centered cubic iron parallel to planes of form $\{111\}$.

A. J. Phillips, working in the Hammond Laboratory, has recently attempted to trace the relationship between these markings and the structure elements which develop on annealing. Deformation figures of striking appearance were found in the altered surface layers of metal shaped by rough grinding with an emery wheel. A sample of copper containing 12.5 per cent. of tin, previously homogenized, developed the regular pattern shown in Fig. 33. Part of a single crystal in cast brass containing 70 per cent. of copper revealed a quite variable distribution of three intersecting sets of bands according to the pattern shown in Fig. 34. Various combinations of bands occur with variable spacing in different parts of the large crystal shown in Fig. 35. Curvature of the bands indicating distortion is also prominent in certain parts of the specimen.

The best proof that these bands are twin bands is that, on annealing, groups of narrow parallel bands merge to form twin bands of ordinary appearance. A very early stage in this process is shown in Fig. 36, a later stage in Fig. 37 and a more perfected stage in Fig. 38.

Theoretically there should be no strain at a simple twin boundary in the face-centered cubic lattice but this is neither true of the extremities nor of the intersections with other bands. Consequently parallel bands may grow into one another from the ends, as is often observed even in the case of the more gradual changes in somewhat stabilized structures at elevated temperatures. This effect is illustrated particularly well by the central group of bands shown in Fig. 39. The selective infiltration

⁴² F. H. Clark: A Study of the Heat Treatment, Microstructure and Hardness of 60-40 Brass. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 276.

⁴³ *Op. cit.*, 299.

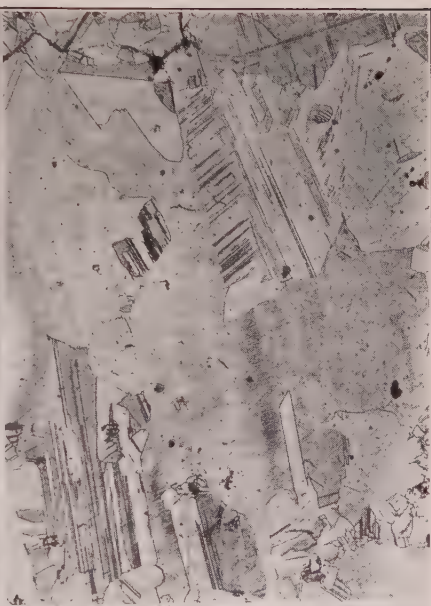
⁴⁴ A recent investigation of the structure of beta brass by Arthur Phillips and L. W. Thelin was reported in the *Journal of the Franklin Institute*, September, 1927.

⁴⁵ F. Osmond and G. Cartaud: *Op. cit.*

37



38



39



40

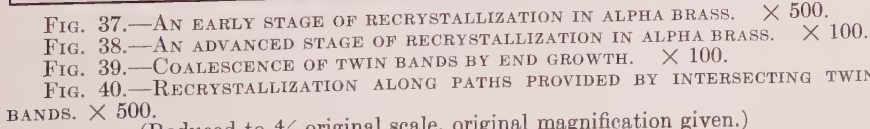


FIG. 37.—AN EARLY STAGE OF RECRYSTALLIZATION IN ALPHA BRASS. $\times 500$.

FIG. 38.—AN ADVANCED STAGE OF RECRYSTALLIZATION IN ALPHA BRASS. $\times 100$.

FIG. 39.—COALESCENCE OF TWIN BANDS BY END GROWTH. $\times 100$.

FIG. 40.—RECRYSTALLIZATION ALONG PATHS PROVIDED BY INTERSECTING TWIN BANDS. $\times 500$.

(Reduced to $\frac{4}{5}$ original scale, original magnification given.)

of a growing band along paths provided by an intersecting set of bands is shown in Fig. 40. Portions of the original crystal and other twin bands are left in the interior of the growing band. This irregular growth, of course, accounts for patches of irregular shape, the so-called recrystallized grains, which according to this view possess the orientations of the original crystal or its four possible twins.

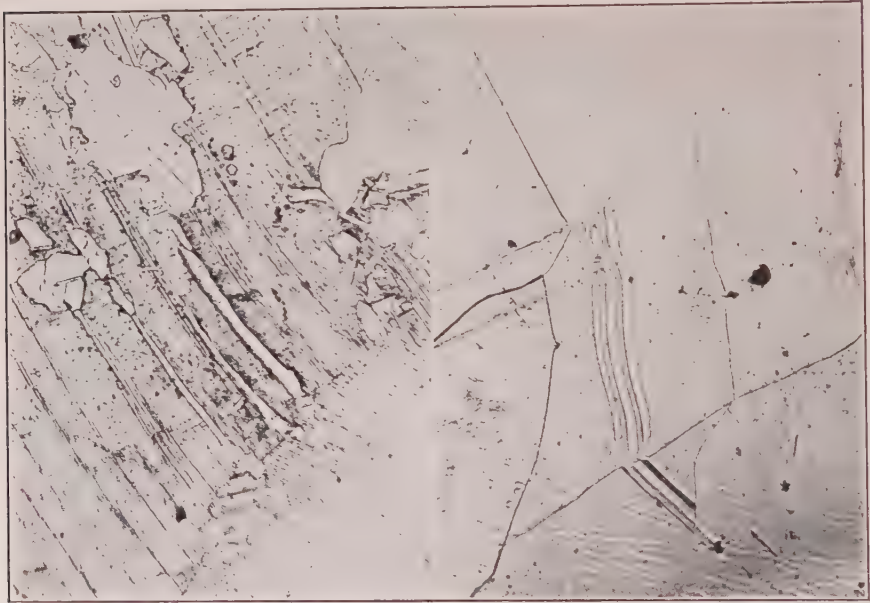


FIG. 41.—FORMATION OF CURVED TWIN BANDS. $\times 500$.

FIG. 42.—CURVED TWIN BANDS IN A FULLY ANNEALED SAMPLE OF ALPHA BRASS. $\times 100$.

(Reduced to $\frac{4}{5}$ original scale, original magnification given.)

General distortion might bring about some deviation from this simple condition in that the parts of a distorted twin band might grow into separate grains of slightly different orientation. That this need not always occur is shown by Fig. 41, in which curved bands have grown together on annealing with a probable readjustment of the atoms to form an unstrained lattice. A good illustration of this effect in a more fully annealed sample may be seen in Fig. 42.

When a crystal which has already been worked⁴⁶ and annealed once is again treated in the same manner, each visible twin band or grain emanating from a twin band is potentially capable of developing a new set of

⁴⁶ It is assumed that all forms of cold working yield twins in most face-centered cubic metals. Even though this is not at once apparent in the microstructure after cold working it is inferred from the numerous twins which are observed after annealing.

bands or grains. The twelve new orientations possible in such a second generation of twins are shown by the open squares in the stereographic projection reproduced in Fig. 43. All orientations are referred to an original plane of form $\{100\}$, the plane of the projection, and the assumption is made that there is no deviation from the reorientation produced exclusively by twinning. If this does not hold each point on the projection might be replaced by a number of points in this general vicinity. A third sequence of working and annealing would be expected to produce a third generation of twins, making a grand total of 53 from a single individual. This process might continue indefinitely.

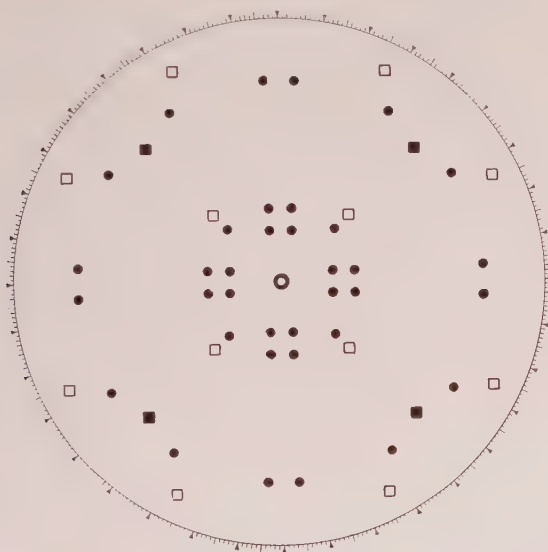


FIG. 43.—STEREOGRAPHIC PROJECTION SHOWING NEW ORIENTATIONS PRODUCED IN A FACE-CENTERED CUBIC CRYSTAL BY TWINNING ALONG ALL POSSIBLE PLANES OF FORM $\{111\}$ THROUGH THREE GENERATIONS.

- = pole of (001) in the original crystal.
- = poles of corresponding planes in twins of the first generation.
- = the poles in twins of the second generation.
- = the poles in twins of the third generation.

It is quite clear that these views give us a new point of departure for considering the effect of various mill schedules on the quality of the product. Thus, a cast material rolled to a certain gage and finished with one anneal would be less uniform and more directional in its properties than the same material annealed several times during the process, although both might look very similar under the microscope. Or, a metal such as aluminum, which apparently fails to develop twin crystals, would be less uniform than a metal such as alpha brass, which twins freely, after comparable treatment.

DISTORTION AT TWIN BOUNDARIES

A complete crystallographic description of any particular form of twinning is possible when the orientations of the crystal and its twin are known. Simple and clarifying assumptions may be made regarding the condition of the lattice in the zone of contact between crystal and twin but the impossibility of directly observing the change in position of the atoms during the operation of twinning and the lack of a method capable of revealing the crystal structure in any localized (boundary) region have left us dependent upon indirect methods of testing these assumptions.

Preston⁴⁷ finds that planes of form $\{111\}$ in the face-centered cubic metals and $\{211\}$ in body-centered cubic metals permit twinning with the least amount of distortion and the most perfect continuity of structure under the fundamental assumption that the components of the twin have in common at least one plane of atoms. Distortion in the sense that atom centers across the twinning plane come closer than the closest distance of approach of atoms in the primitive material would be entirely absent in this ideal form of face-centered cubic twinning, but would be present to a slight degree even in this most favorable form of body-centered cubic twinning.

A possible form of distortion in the twinning of zinc along planes of form $\{10\bar{1}2\}$ was shown by Mathewson and Phillips⁴⁸ and Fig. 44 represents the development of a similar plan involving an intersection between two conjugate bands. One of the planes of form $\{10\bar{1}2\}$ is maintained in each twin and the twinning is supposed to occur by progressive slip together with a slight secondary adjustment, along the neighboring planes of this form. There does not appear to be any plane that would permit twinning without distortion in hexagonal close-packed metals even when the axial ratio corresponds to close packing of spheres.

If both parts of the crystal move as a whole each time a layer is added to a simple twin band, the distortion may be confined very closely to the boundaries as shown in the original figure, but if a twin lamella merely bridges a gap between two parts of the same crystal⁴⁹ there must be a zone of distortion in which the horizontal rows of atoms at the right of the band rise to their natural level in the unaltered crystal. This condition is represented in Fig. 45. The very common tendency of twins in zinc, cadmium, and tin to taper probably represents a natural tendency to avoid abrupt transitions of structure and hence strongly localized distortions in any part of the material. An estimate of the

⁴⁷ G. D. Preston: The Formation of Twin Metallic Crystals. *Nature* (1927) **119**, 600.

⁴⁸ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. of Metals Div. A.I.M.E.* (1927) 186.

⁴⁹ Twins produced by local indentation, for example.

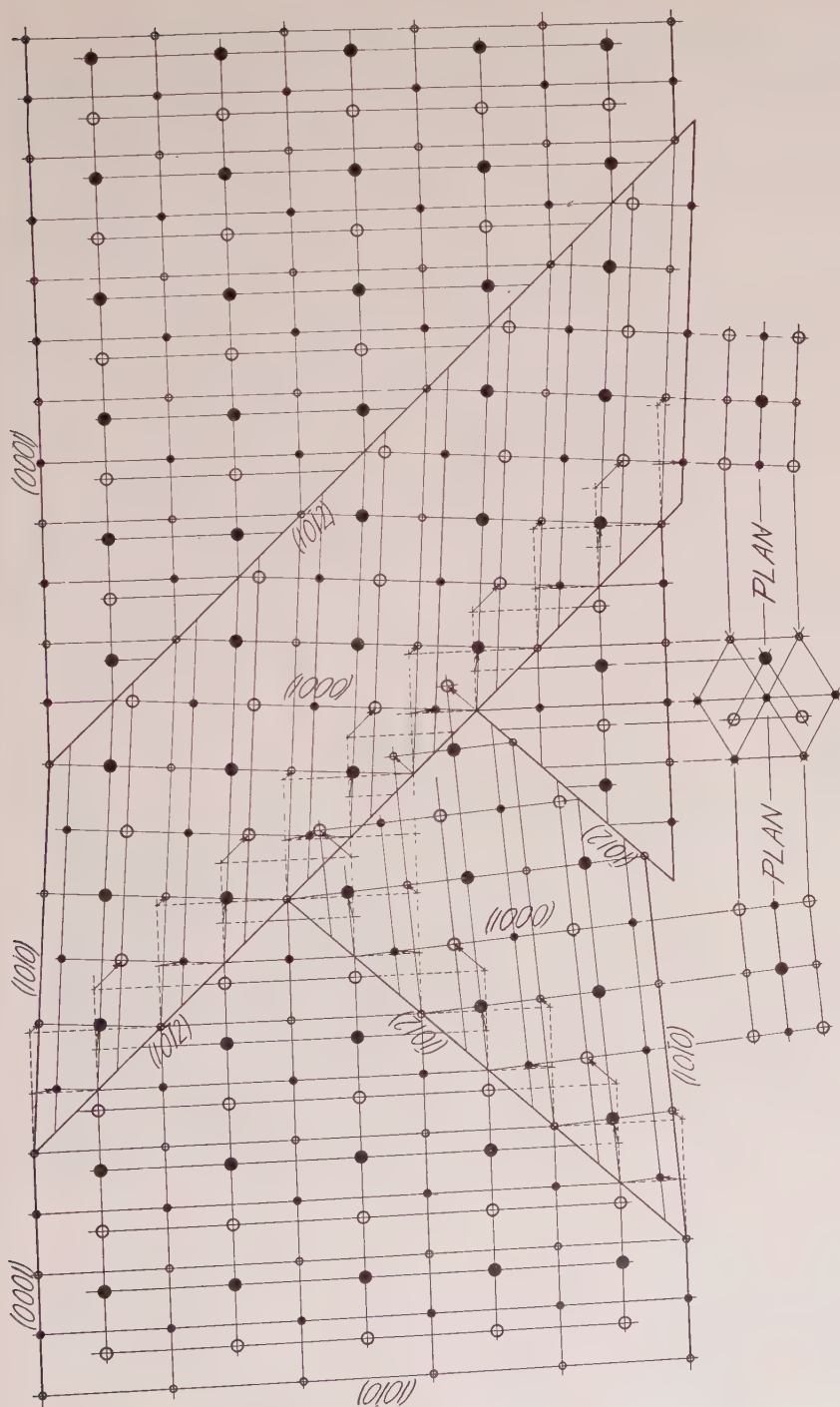


FIG. 44.—CROSS-SECTION THROUGH TWIN BANDS IN ZINC. TWINNING PLANES PERPENDICULAR TO THE PLANE OF THE SECTION. SHOWS POSSIBLE FORMS OF DISTORTION AT TWIN BOUNDARIES.

results which may be secured in this manner may be made by comparing Fig. 45 with Fig. 46.

The examples already introduced leave little room for doubt that simple twinning within a crystal may generate twin boundaries either

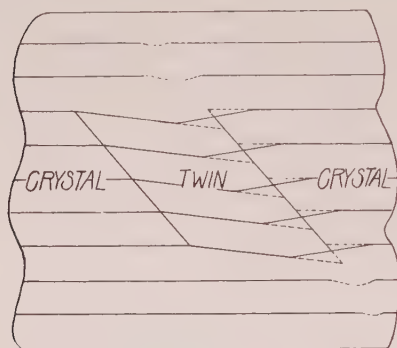


FIG. 45.—POSSIBLE ZONES OF SEVERE DISTORTION AT THE BOUNDARIES OF AN INTERNAL TWIN BAND.

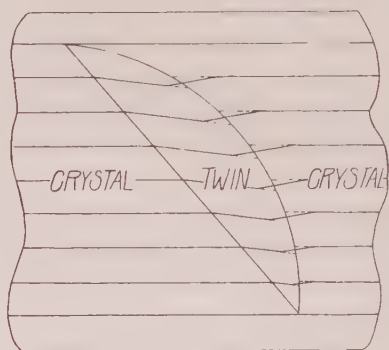


FIG. 46.—GRADUATED DISTORTION AT THE BOUNDARIES OF A TAPERED INTERNAL TWIN BAND.

free from strain or accompanied by strain varying greatly in amount and distribution according to the forms of crystal lattice and twinning plane and the configuration of the twinned area.

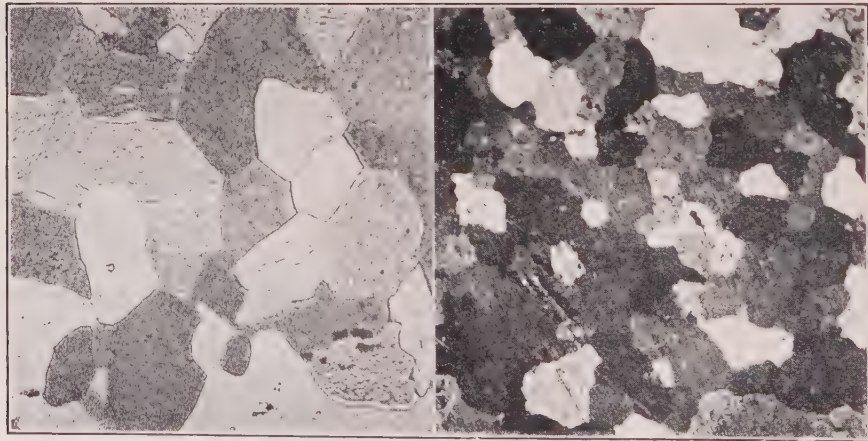


FIG. 47.—WORKED AND ANNEALED ZINC. FIG. 48.—WORKED AND ANNEALED TIN.

Small twins with unstrained boundaries often grow into large ones, as is so commonly observed in the annealing of copper and its alpha solutions. I can find no evidence that such a process occurs in the case of twins with strained boundaries, although certain large twins of this character may retain their original shape on annealing, as observed by

Mathewson and Phillips in zinc⁵⁰ and McKeehan in iron.⁵¹ Commonly, small twins with strained boundaries fail to retain the banded structure and ultimately produce grains with irregularly shaped boundaries, as in Fig. 32 from Krivobok's work on iron,⁵² Fig. 47 representing worked and annealed zinc, and Fig. 48 representing worked and annealed tin. These facts give support to the fundamental assumption of a plane

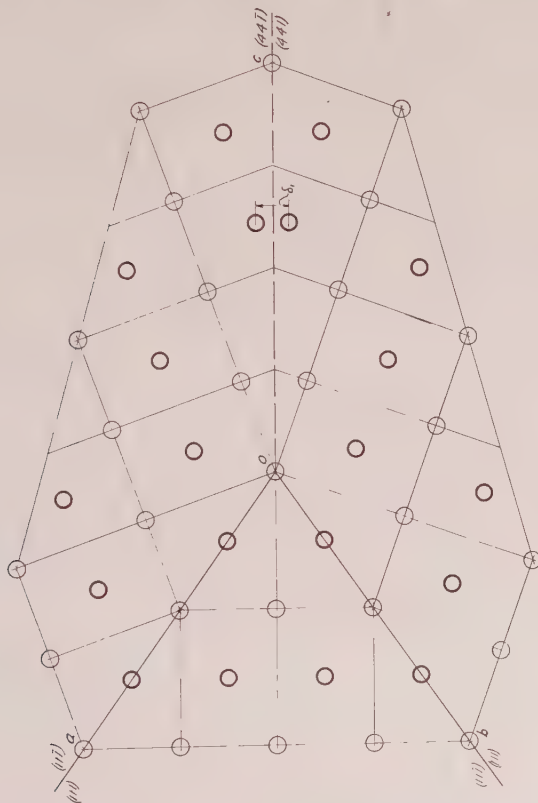


FIG. 49.—PROJECTION OF PART OF A FACE-CENTERED CUBIC CRYSTAL TWINNED ALONG TWO PLANES OF FORM $\{111\}$ WHICH MEET AT AN ANGLE OF $70^\circ 32'$. PLANE OF THE PROJECTION PERPENDICULAR TO THE LINE OF INTERSECTION OF THESE PLANES.

common to both components of a twin and the accompanying interpretation of strain.

A close connection between twinning and recrystallization in copper and alpha brass was observed in the experiments of A. J. Phillips. It was shown that the narrow indelible markings (etch bands) resembling Neumann bands in ferrite coalesce directly into twin bands of ordinary

⁵⁰ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Metals Div. A.I.M.E.* (1927) 183.

⁵¹ L. W. McKeehan: *Op. cit.*

⁵² V. N. Krivobok: *Op. cit.*

appearance. The frequent occurrence of new orientations (recrystallization) was undoubtedly due to a lack of perfect homogeneity within the bands as a whole. While no evidence could be adduced to prove the absence of distortions due to causes other than twinning, the obvious disturbance caused by the interpenetration of two sets of bands led to

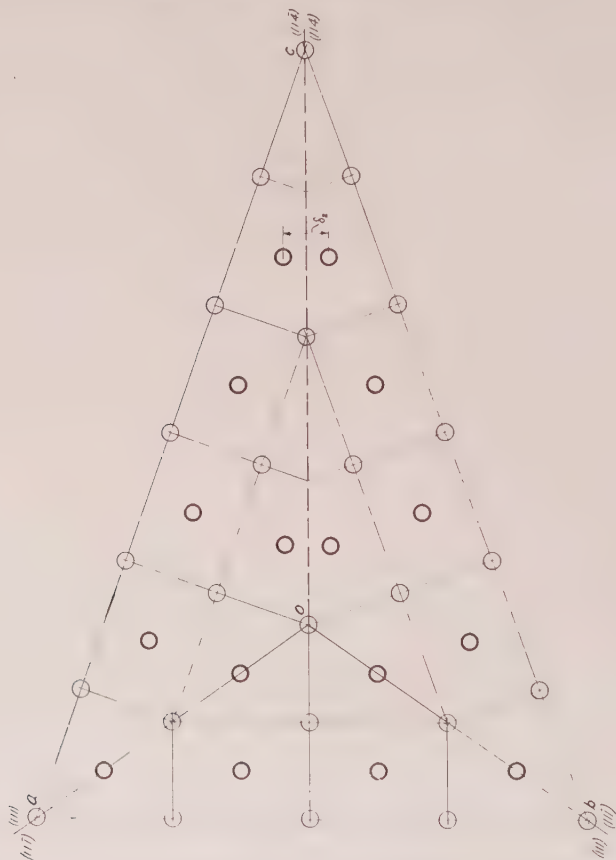


FIG. 50.—PROJECTION OF PART OF A FACE-CENTERED CUBIC CRYSTAL TWINNED ALONG TWO PLANES OF FORM $\{111\}$ WHICH MEET AT AN ANGLE OF $109^{\circ} 28'$. PLANE OF THE PROJECTION PERPENDICULAR TO THE LINE OF INTERSECTION OF THESE PLANES.

the belief that such intersections were at least a principal source of the distortion which is responsible for recrystallization.

I am indebted to my colleague, L. W. McKeehan, for the following analysis of the twin relationships in a face-centered cubic crystal.

Fig. 49 is a projection of a portion of the crystal twinned along two planes of form $\{111\}$ which make an angle of $70^{\circ} 32'$. The plane of the projection is perpendicular to the line of intersection of the two composition planes, shown at oa and ob . Since oa and ob are planes of form

$\{111\}$ their intersection is a line of form $[110]$. The plane of projection is therefore of the form $\{110\}$. The two different twins aoc and boc , which were derived from the crystal aob , are mirror images of each other in the plane oc , of form $\{441\}$ and the closest distance of approach of atom centers, δ_1 , is only 0.33 of the least distance before twinning. Fig. 50 is a similar projection in which the pairs of twinning planes make an angle of $109^\circ 28'$. In this case the new composition plane, oc , between the twins becomes of the form $\{411\}$ and the closest distance of approach of atom centers is δ_2 , or 0.47 of the normal distance before twinning. Both cases, therefore, require a great amount of distortion, as was suspected from the experimental evidence.

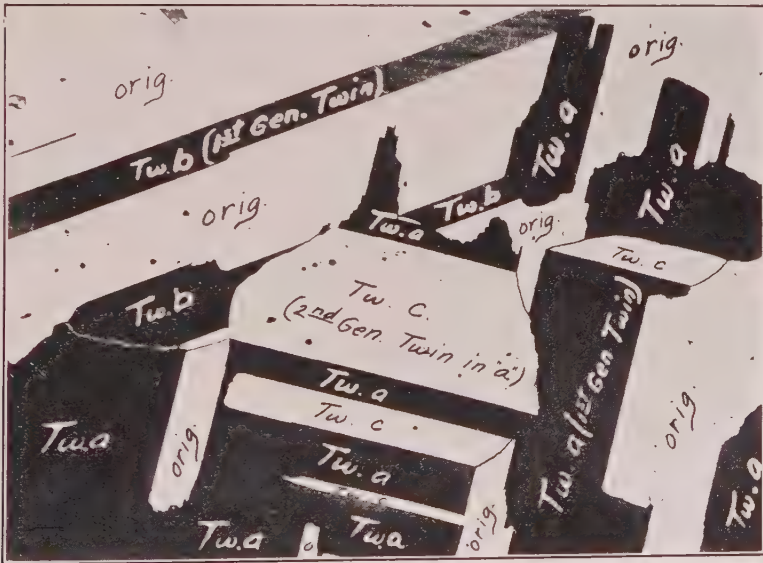


FIG. 51.—TWO GENERATIONS OF TWINS IN A SINGLE BRASS CRYSTAL.

From these considerations it is evident that the absence of distortion in the vicinity of the composition plane between a crystal and its twin does not imply a similar absence of distortion at the surfaces of contact between various twins formed primarily within the original crystal or secondarily within these twins of the first generation.

The stereographic projection given in Fig. 43 exhibits the entire group of 53 orientations which may be formed by multiple internal twinning along planes of form $\{111\}$ through three generations in a face-centered cubic crystal.

Probably many of the possible combinations embraced in this projection with great diversity in the amount of distortion at the boundaries are encountered during the succession of cold working and annealing operations to which metals are frequently subjected. That twins of at

least two generations may be found together with a residue of the original crystal in a fully annealed product is proved by the examination made by A. J. Phillips⁵³ of the crystal shown in Fig. 51. Here, *orig.* or *o* is the original crystal, *Twa* and *Twb* are twins of the first generation and *Twc* is a twin of the second generation in *Twa*.

It is believed that many and perhaps most of the new orientations formed during the recrystallization of these face-centered cubic metals are due to complex twinning resulting in strained boundaries which permit growth and readjustment in various forms.

COMPARATIVE FUNCTIONS OF TWINNING AND SLIP IN THE GENERAL PROCESS OF PLASTIC DEFORMATION

Simple twinning, unaccompanied by slip, does not provide for any considerable change in the dimensions of a crystal and cannot account for the great amount of plasticity which is observed in the ordinary operations of rolling, drawing, etc. The possibilities of twinning and slip in this respect are compared in Figs. 52 and 53. These sketches represent sections perpendicular to a twinning plane, *t*, and a slip plane, *s*, respectively. The initial thickness is represented by the vertical distance, *d*.

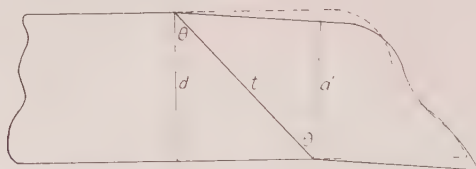


FIG. 52.—CHANGE IN THICKNESS BY TWINNING. TWINNING PLANE PERPENDICULAR TO PLANE OF SECTION.

Twinning across the entire section, as shown in Fig. 52, causes an equal angular displacement of the upper and lower surfaces of the crystal from the horizontal plane and changes the thickness to *d'*. There is, of course, a corresponding change in orientation. If Θ represents the angle between the twinning plane and the vertical plane and, similarly, Θ' , the angle between the twinning plane and the plane perpendicular to the crystal surfaces after twinning, the expression,

$$\frac{d}{d'} = \frac{\cos \Theta}{\cos \Theta'}$$

gives the ratio of thickness before and after twinning.

The angles Θ and Θ' can be changed only by changing the initial orientation.

In the case of simple slip, as shown in Fig. 53a, the surfaces of the crystal move out of the horizontal plane but acquire a stepped configura-

⁵³ A. J. Phillips: *Op. cit.*

tion which approaches a plane surface as the number of slip planes contributing to the total displacement becomes infinite. In reality this number is limited by the finite distance between consecutive planes of the form under consideration. The ratio of thickness before and after the deformation, as in the case of twinning, is given by the expression

$$\frac{d}{d'} = \frac{\cos \Theta}{\cos \Theta'}$$

However, the angle Θ' , in this case can be increased, as shown in Fig. 53b, by increasing the amount of slip. In this way, the thickness may be continually reduced as long as the slipping process can be made to operate.

Simple slip along one set of planes changes the plane of the surface without changing the orientation. Doubtless many movements of this

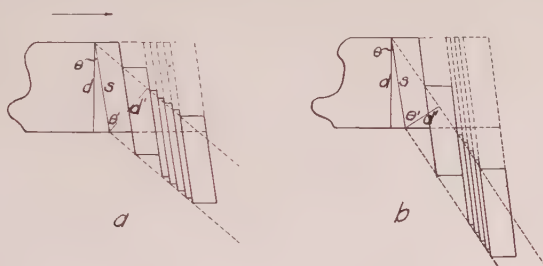


FIG. 53.—CHANGE IN THICKNESS BY SLIP. SLIP PLANE PERPENDICULAR TO PLANE OF SECTION.

sort take place during plastic deformation of an aggregate of crystals of random orientation. Unless a principal component of stress remains parallel to the moving surface as simple slip proceeds, which would appear to require some special supporting or adjusting mechanism, the crystal must yield in another direction. This may bring into play another set of slip planes or a set of twinning planes if either are available, while in the absence of such favorable conditions progressive curvature of the slip planes, or certain localized lattice distortions, must occur as the movable surface is forced continually into line with the direction of stress.

It was pointed out by Jeffries and Archer⁵⁴ that the wedge-shaped fractures observed by Sykes in 1921⁵⁵ in molybdenum wires were probably

⁵⁴ Zay Jeffries and R. S. Archer: Effect of Temperature, Pressure and Structure on Mechanical Properties of Metal. *Chem. & Met. Eng.* (1922) **27**, 747.

⁵⁵ W. P. Sykes: Effect of Temperature, Deformation, Grain Size and Rate of Loading on Mechanical Properties of Metals. *Trans.* (1920) **64**, 780.

produced by coöperative movements of the first kind, namely, slip along conjugate planes inclined 45° to the axis of the wire.

Later Goucher⁵⁶ in a series of three papers very carefully analyzed these wedge-shaped fractures through single crystals of tungsten and ascribed them to slip along conjugate planes of form $\{211\}$ in the direction $[111]$. Even in the case of the most symmetrical wedges, which would appear to favor slip in its simplest form, rather large amounts of distortion were observed, which in the words of the author "affected the inclination of the crystal planes in the direction of slip, but produced no marked change in the atomic spacings." This indicates that severe distortion which might be visualized as curvature of the slip planes in the above sense actually results in fragmentation, or disintegration of the crystal into small lattice units arranged on curved surfaces.

Taylor and Elam⁵⁷ working with aluminum, and later Elam⁵⁸ with other face-centered cubic metals and alloys, have described slip along single and conjugate planes of form $\{111\}$ in single crystals of these materials with characteristic changes in orientation as the slip planes tend to reach a position of equilibrium in conformity with the loading conditions adopted. No particular theory of lattice distortion was favored by these authors.

On the other hand, Polanyi, in a number of communications,⁵⁹ vigorously asserts that cold working in general produces lattice distortion by a combined process of slip and bending (*Biegegleitung*) which was first observed in zinc by Mark, Polanyi and Schmid.⁶⁰ If only one set of slip planes can operate in the case of zinc, tensile stress in the direction of the arrow in Fig. 53 must either distort the lattice (by *Biegegleitung*) or bring some form of compensatory movement into play. Mathewson and Phillips⁶¹ suggested that twinning across the slip planes might satisfy

⁵⁶ F. S. Goucher: On the Strength of Tungsten Single Crystals and Its Variation with Temperature. *Phil. Mag.* (1924) **48**, 229.

Studies on the Deformation of Tungsten Single Crystals Under Tensile Stress. *Phil. Mag.* (1924) **48**, 800.

Further Studies on the Deformation of Tungsten Single Crystals. *Phil. Mag.* (1926) **2**, 289.

⁵⁷ G. I. Taylor and C. F. Elam: The Distortion of an Aluminum Crystal during a Tensile Test. *Proc. Roy. Soc.* (1922 3) **102A**, 643; also The Plastic Extension and Fracture of Aluminum Crystals. *Proc. Roy. Soc.* (1925) **108A**, 28.

⁵⁸ C. F. Elam: Tensile Tests of an Aluminum Zinc Alloy. *Proc. Roy. Soc.* (1925) **109A**, 143; also Tensile Tests of Large Gold, Silver and Copper Crystals. *Proc. Roy. Soc.* (1926) **112A**, 289 and Tensile Tests on Alloy Crystals. *Proc. Roy. Soc.* (1927) **115A**, 133 and (1927) **116A**, 694.

⁵⁹ For instance: Kristalldeformation und Verfestigung. *Zeitsch. Metall.* (1925) **17**, 94.

⁶⁰ H. Mark, M. Polanyi and E. Schmid: *Op. cit.*

⁶¹ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Metals Div. A.I.M.E.* (1927) 144.

this condition. This has recently been denied by Wilson and Hoyt,⁶² although possibly on insufficient grounds.⁶³

Whatever the relative functions or interrelationship of slip and twinning in zinc crystals under simple forms of static loading, there is no doubt that these two processes coöperate and are mutually indispensable in facilitating the plastic deformation of zinc by ordinary methods of cold working.

The first stage of rolling on a basal surface already described in some detail is especially significant in this respect. The reduction in thickness in this experiment (6.98 per cent.) corresponds almost exactly to the amount required by complete twinning along planes of form $\{10\bar{1}2\}$ and very large portions of the specimen are found entirely converted to the twin orientation. This corresponds to the condition shown in Fig. 52 requiring the twinned part of the crystal to develop surface planes inclined to the original surface and at once suggests that a forward portion of the specimen tilts downward as it twins between the rolls and thereupon emerges



FIG. 54.—PYRAMIDAL TWINNING IN A ZINC CRYSTAL FOLLOWED BY BASAL SLIP IN TWIN LAMELLAE. TWINNING AND SLIP PLANES PERPENDICULAR TO PLANE OF SECTION.

at the proper angle to the material just entering the rolls. Other parts of the surface, however, have undoubtedly left the rolls in a horizontal plane in spite of twinning, a condition which seems to require slip according to some plan similar to the one shown⁶⁴ in Fig. 54. The thickness measured in the vertical plane after twinning along $(01\bar{1}2)$ planes and basal slip in the twinned material would be given by the expression, $d'' = d \frac{\cos \theta'}{\cos \theta} \cos (\theta' - \theta)$ in which $\theta = 42^\circ$, $56'$, $\theta' = 47^\circ$, $4'$ and d , the initial thickness, is taken as unity. This represents a reduction in the thickness of 7.21 per cent., which is a little more than the amount attained in the experiment.

The possibility of prismatic slip through residual lamellae of the original crystal is illustrated at p in the figure. This would introduce transverse strain, which might account for some of the twinning across such bands. Actual observations in rolling show that twinning does not

⁶² T. A. Wilson and S. L. Hoyt: X-ray Analysis of Plastic Deformation of Zinc See p. 241.

⁶³ Cf. discussion of Wilson and Hoyt's paper by L. W. McKeehan.

⁶⁴ In order to simplify the discussion it is assumed that the twinning planes are perpendicular to the exposed vertical section representing the direction of rolling in these experiments.

follow a single set of planes all the way through the specimen, as in Fig. 54, but is distributed among two sets of conjugate planes, closely parallel to the principal shear components of stress, one of them brought into play by the action of the upper roll and the other by the lower roll. This condition is illustrated in Fig. 55. When the end of the specimen gets the full pinch of the rolls it is twinned from top to bottom as represented in the shaded area of Fig. 55*a*. On further progress through the rolls twinning might spread out along the conjugate planes (0112) and (0 $\bar{1}$ 12) without causing one triangular zone to invade the other, by pushing the end blocks along the (shaded) slip planes of form {0001} to generate new horizontal surfaces as shown in Fig. 55*b*.

The symmetrical effect shown in these two sketches has not been observed. Irregularities, such as eccentric loading or variation in composition, soundness or crystalline perfection of the metal commonly alter the distribution of stress and give rise to variously complicated structures of the type shown in Fig. 55*c*.

In case the thickness of the crystal is not reduced the full 6.98 per cent.,⁶⁵ which corresponds to complete twinning from top to bottom, alternate lamellae of the original crystal and its twin will be found as in Fig. 55*d*. The conditions shown in Figs. 55*c* and 55*d* may be combined to yield the highly complicated condition shown in Fig. 55*e*. This is quite representative of the structures actually observed.

As the crystal rolls out, twinning continues to feature the microstructure of the product and there is clear evidence of slip on the polished sides of a specimen. It seems probable that both twinning and slip are vitally concerned in the process, the former offering a rational plan for a shifting of the orientation within the mass to meet the stress conditions encountered from time to time and the latter providing for most of the plastic thinning of the crystal.

It is possible to imagine a unique combination of twinning and slip which would permit a succession of transformations from original crystal to twin and back to original crystal, with a reduction in thickness at each stage of the process. The central section of Fig. 56 shows the positions of the atoms in a twinned layer of a zinc crystal with twinning plane perpendicular to the plane of the section. The change from original position to twin position of all atoms in the first four rows parallel to the row held in common by the crystal and its twin is indicated by arrows. For comparison a similar set of five rows free from these construction details is shown by dotted lines a short distance to the right. The five rows constitute a block bounded by two geometrically similar planes and the action in this block may be considered representative of the process as a whole. It is believed that incipient or fractional slip

⁶⁵ $\frac{1.862 - \sqrt{3}}{1.862} \times 100.$

in these rows brings the atoms near enough to the positions they would occupy in the twin to determine an automatic and instantaneous completion of the twinning process.

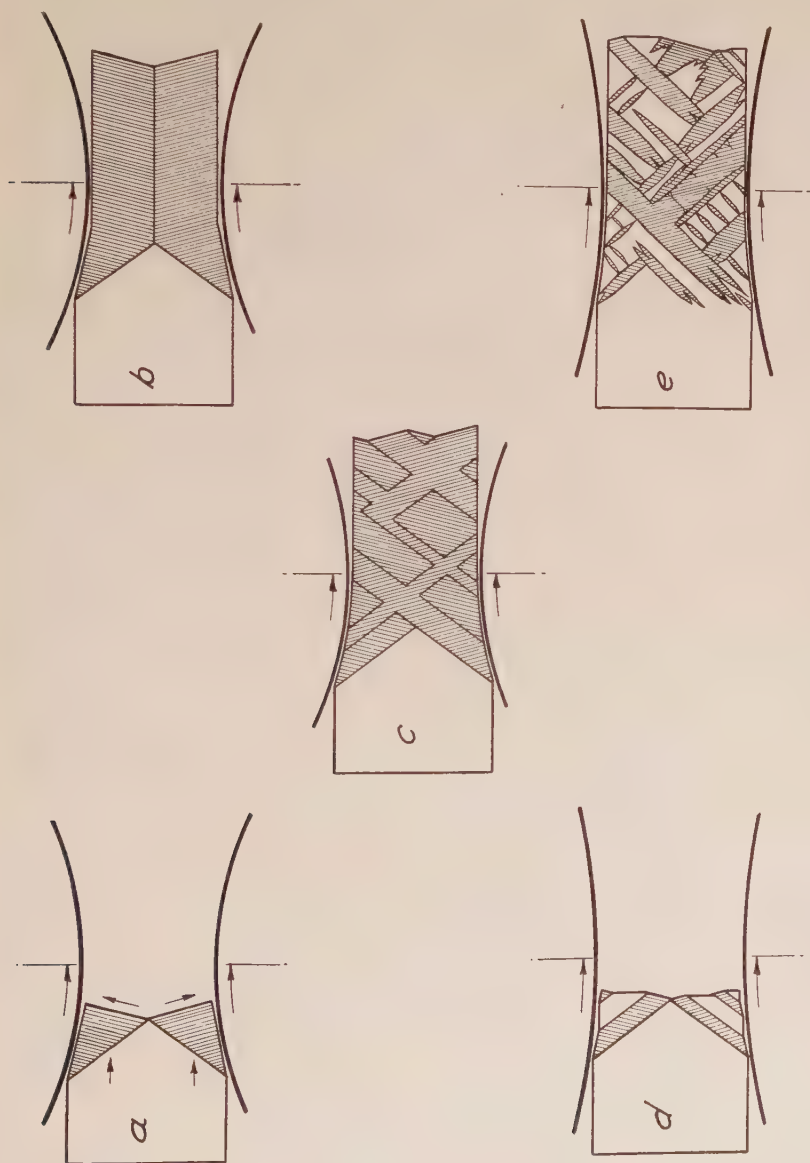


Fig. 55.—TWINNING AND SLIP IN A ZINC CRYSTAL BY ROLLING. SECTION PERPENDICULAR TO (0001) AND (0112). FULL TWINNING REDUCTION IN *a*, *b*, AND *c*; PARTIAL REDUCTION IN *d* AND *e*.

The general effect of this change is to deform the block by lowering its forward boundary (the fifth row of atoms) an amount corresponding to the fractional slip shown just below the first figure 5 in the sketch and adjusting the positions of the atoms in the interior.

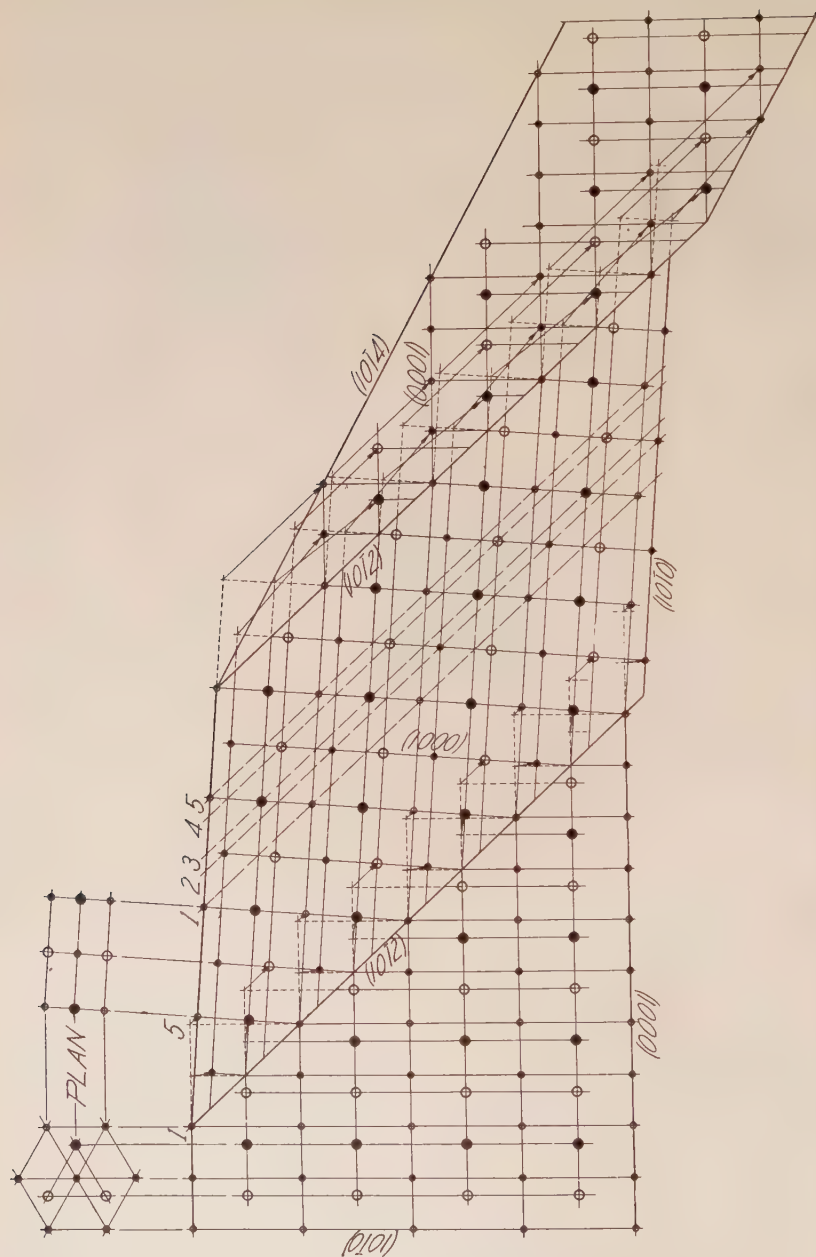


FIG. 56.—SIMPLE TWINNING AND A CONJECTURED RETURN TO THE ORIGINAL ORIENTATION WITH PROGRESSIVE REDUCTION IN THICKNESS. TWINNING PLANES PERPENDICULAR TO PLANE OF SECTION.

If now, we deform a similar block in the twin by lowering its forward wall far enough to complete a fractional slip of the above character and suitably readjust the atoms in the interior, the orientation of the original crystal will result with a very considerable reduction in thickness as shown in the right-hand section of the sketch.

The first part of the process just described seems probable as it moves the atoms much less than would correspond to a full slip in any case and is quite in harmony with the recorded observations on twinning. On the other hand, there is no evidence that the last part of the process ever occurs. It is perhaps improbable on account of the very considerable relative displacements of the atoms.

We have seen that twinning is capable of introducing strain and thereby supplying the incentive for recrystallization. From a crystallographic point of view this form of lattice reconstruction is more systematic and less arbitrary and quite likely of more frequent occurrence than the other alterations in crystal structure involving distortion, such as rotation during slip around an axis perpendicular to the slip plane or around an axis lying in the slip plane (*Biegegleitung*), which have been observed under special conditions and are supposed to occur freely in the case of severe deformation.

POSTULATES CONCERNING TWINNING IN RELATION TO THE PLASTIC DEFORMATION OF METALS

1. When in the inhomogeneous deformation of a metal by slip combined with distortion, the atoms in certain zones reach positions more nearly approximating equilibrium positions in a possible twin than in the original crystal, twin lamellae will be formed with partial relief of stress and the residual distortion will be distributed in harmony with the geometrical requirements of each special case.

2. By far the great majority of the metals are subject to structural alteration of this character.

3. Under slowly applied loads there is a minimum occurrence of the continuous distortion from plane to plane required to initiate twinning, owing to the tendency toward premature slip along "weak" planes of variable spacing depending upon the concentration of impurities or the operation of other factors which may affect the cohesion between planes.

4. Under impact loading a given small displacement is momentarily distributed among many planes, thus disturbing the equilibrium of large numbers of atoms and potentially favoring the formation of sizable twin bands.

5. The distortion around simple twin bands wholly enclosed within the original crystal may be confined to the ends as distinguished from the parallel sides bounded by twinning planes and this brings about end

growth on annealing which may spread along the sides. In other cases distortion may exist at the composition planes and bring about direct lateral growth.

6. Both the quantity and the size of deformational twins are greatly affected by the kind of deformation and the purity of the metal.

7. Distortion and thermal instability are especially pronounced in the vicinity of faults or direct intersections where twin bands enter into conflict with one another.

8. One form of recrystallization is essentially granulation produced by irregular and competitive growth of interstratified twin lamellae which are here termed crystallographic fragments in that they cannot be fitted together without distortion in spite of their crystallographic relationship through the parent crystal.

9. Recrystallization in the absence of twinning is a similar reaction between lamellae (fragments) formed by inhomogeneous distortion during slip, *e. g.*, variable rotation of the slip planes. This leads to less pronounced changes in orientation from grain to grain than is effected by twinning.

10. In conformity with the conception of recrystallization expressed in (8) and (9), diversity of orientation after a succession of deformational and annealing treatments is due to multiple internal twinning, rotation during slip or some combination of these two causes depending upon the nature of the metal, the initial orientation of the crystals, and the kind of deformation.

Physical Characteristics of Commercial Copper-zinc Alloys

BY W. H. BASSETT* AND C. H. DAVIS†, WATERBURY, CONN.

(Detroit Meeting, September, 1927)

ALTHOUGH brasses and bronzes have been made for ages, a systematic study of their physical properties has been carried out only during the years of the present century. Among these properties may be included those which are to be detected by means of microscopic examination; in other words by the science of metallography.

The earlier workers in this field, both in this country and abroad, gave their attention to steel. When the senior author explored the situation in 1902, there was little encouragement to be found in undertaking the study of the non-ferrous alloys. A start was made, and the metallography of the brasses and bronzes, as well as of the copper-nickel-zinc alloys developed materially under his direction. Annealing experiments were begun in 1902, and in the succeeding years the effect of temperature, and the influence of previous working, on the grain size of brass were studied. The conclusions so well known and widely published today were largely reached during those earlier years. In 1905 the first complete annealing series were made. By this it is meant that brass and copper sheet, 5 B & S Nos. hard, was machined into tensile test specimens, then annealed under accurate control for 30 min. at temperatures up to the melting point of the material. Various determinations were made, including tensile strength and elongation in 2 in.

There rapidly followed similar series on all of the copper-zinc alloys from 100 to 60 per cent. copper, on the bronzes, cupronickels, and on copper-zinc-nickel alloys. At this point there was published by Grard, in October, 1909,¹ the very comprehensive and complete work on the tensile properties of cartridge brass, 90-10 copper-zinc, and electrolytic copper. The excellent photomicrographs in that paper illustrated the changes in structure produced by cold rolling as well as by annealing at different temperatures, but where Grard's work was confined to copper and to two alloys, the investigations in this laboratory have been over the entire fields of the commercial copper-zinc alloys, copper-tin alloys, representative copper-nickel and copper-nickel-zinc alloys as well as aluminum bronzes and others of a more special nature.

* Technical superintendent and metallurgist, The American Brass Co.

† Assistant metallurgist, The American Brass Co.

¹ L. Grard: Laiton à Cartouches. Laiton à Balles. Cuivre Électrolytique. *Revue de Métallurgie* (1909) 6, 1069.

The data and plots given in this paper are arranged to constitute a summary, enabling one at a glance to see the physical properties of the copper-zinc alloys to 62 per cent. copper. The data employed in making these plots are concise but are of so great a volume that they are not published in detail. The characteristics shown are tensile properties, hardness and grain size, both in picture and in numerical values.

Valuable data on brasses and bronzes have been published. Guillet, in 1914,² gave the results of an investigation of the tensile properties of cold-rolled and hot-rolled brasses 100 to 56 per cent. copper. The studies were limited, however, to simple treatments, whereas it is now proposed to show the characteristics of brass after various reductions by cold working, as well as of brass annealed over a wide range of temperatures. Furthermore, the treatment will be that given on a commercial scale rather than that limited, as in the case of Guillet, to small laboratory castings. The work of Mallet,³ Thurston,⁴ Charpy,⁵ and Bancroft and Lohr⁶ was not as comprehensive as the work of Guillet and that of Grard. The more recent investigations on the copper-zinc system and the physical characteristics of the alloys from 100 to 60 per cent. copper have been published through the medium of scientific societies and journals.

The knowledge gained by the study of the characteristics of the alloys led to a facility in interpreting the causes of failure in the working of metals as well as in recommending materials for various uses, especially for engineering purposes. Still more it showed the necessity of a close control of the purity of the raw materials entering in the alloys; consequently the studies were extended to cover all of the important brands of copper, nickel and zinc then available. Twenty-six brands of copper and about 35 of zinc were most carefully and completely analyzed during the years 1912 to 1914. A large quartz spectrograph, the first, we believe, to have been used in this connection, was employed in furthering the discoveries of the impurities in the raw material. Complete tests were conducted to ascertain the physical characteristics of all of these coppers, having in mind the effect of such impurities on the quality of the alloys into which the copper would go.

All through these years tensile-strength data were assembled, and the resistance of the alloys to fatigue, to alternate bending, to friction, and to corrosion was studied. Some of the results have been published.

² M. L. Guillet: *Nouvelles Recherches sur les Alliages de Cuivre et de Zinc. Revue de Métallurgie* (1914) **11**, 1094.

³ R. Mallet: On the Physical Properties and Electro-chemical and other Relations of the Alloys of Copper with Tin and Zinc. *Phil. Mag.* (1842) **21**, 68.

⁴ R. H. Thurston: *Materials of Engineering*, Pt. 3. John Wiley & Sons.

⁵ M. G. Charpy: *Recherches sur les Alliages de Cuivre et de Zinc. Bull. de la Société d'Encouragement pour l'Industrie Nationale* (1896) **1**, 180.

⁶ W. D. Bancroft and J. M. Lohr: The Tensile Strengths of the Copper-zinc Alloys. 8th Intl. Congress of Applied Chemistry (1912) **2**, Sec. 2, 9.

PHYSICAL CHARACTERISTICS OF COPPER

To illustrate the difference in copper from different sources and containing different impurities, Fig. 1 has been prepared. This shows the result of annealing strips 0.050 in. thick rolled 10 B & S Nos. hard from a pure electrolytic copper and a high-grade lake copper containing 25.3

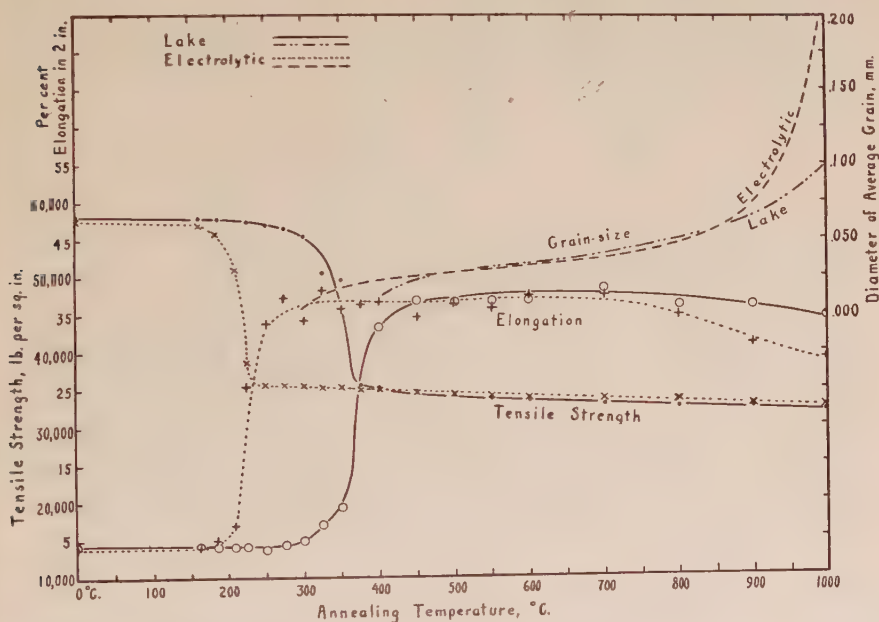


FIG. 1.—COMPARISON OF A LAKE AND AN ELECTROLYTIC COPPER. TENSILE STRENGTH, ELONGATION AND GRAIN SIZE OF 0.050-IN. SHEET, 10 B & S Nos. HARD, ANNEALED AS NOTED.

oz. of silver per ton. The lake behaves like an alloy while the electrolytic maintains the characteristics of pure copper. The rapid change, due to annealing, begins at 200° C. for the purer metal and at about 350° C. for the argentiferous copper. The grain size of the pure copper after recryst-

TABLE 1.—Analyses of Copper

	Electrolytic, Per Cent.	Lake, Per Cent.
Copper.....	99.9565	99.8762
Silver.....	0.0005	0.0868
Arsenic.....	0.0025	0.0020
Antimony.....	0.0011	0.0026
Lead.....	0.0007	0.0003
Iron.....	0.0006	0.0020
Conductivity annealed.....	100.54	99.82

Oz. per ton 25.34

tallization changes very slowly with increasing temperature up to about 800° C., when the small crystals suddenly coalesce into very large irregular ones. This temperature corresponds roughly with a change in direction of the elongation curve. This is characteristic of pure copper.

The lake copper gradually increases in grain size with increasing temperature, following in a general way the grain growth observed in copper-zinc and other copper alloys. The strength curve remains flat after the rapid change, as is general with copper, and the elongation curve about 700° C. falls similarly to that of pure copper, but not as rapidly.

PHYSICAL PROPERTIES OF BRASS

The copper-zinc alloys, as is well known, vary in color from that of copper through the reddish bronzes to the bright yellow of the 66-34 copper-zinc mixture. Just below this point, however, there is a change in color not always appreciated. The beta constituent, which is reddish in color, causes an increasing reddening of the metal as the pure beta region is approached. With the appearance of the gamma phase, at about 50 per cent. copper, the alloys become gray, and are white at the pure gamma area (40 per cent. to 31 per cent. copper).

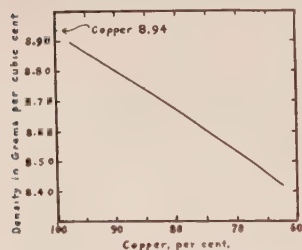


FIG. 2.—RELATION BETWEEN DENSITY AND COPPER CONTENT OF COLD-ROLLED COPPER-ZINC ALLOYS. (BUR. STDS. *Sci. Paper* 410.)

The specific gravity of the alloys decreases at a constant rate, as shown by Fig. 2.⁷ The test specimens for the specific-gravity determinations were those prepared under the direction of the authors, as were those used for the thermal expansion investigation conducted at the Bureau of Standards.⁷ The relations between the instantaneous coefficient of expansion and the copper content of the alloys is shown in Fig. 3.

TENSILE TESTS

The tensile strength and the percentage elongation in 2 in. of the copper-zinc alloys from 100 to 62 per cent. copper are shown in Figs. 4 and 5. The data are upon metal commercially prepared, cold rolled, with a reduction of 44 per cent. (approximately 5 B & S Nos. hard) and upon similar specimens milled to the final shape before annealing to temperatures from 200° to 850° C., or higher.

Copper and 11 alloys were employed in gathering the data for these two plots. The points are taken from smoothly drawn curves of the

⁷ P. Hidnert: Thermal Expansion of Copper and Some of Its Important Industrial Alloys. Bur. Standards *Scientific Paper* No. 410.

several alloys, such as those shown for the 75-25 copper-zinc alloy, Fig. 6. The practice throughout has been to anneal the machined test speci-

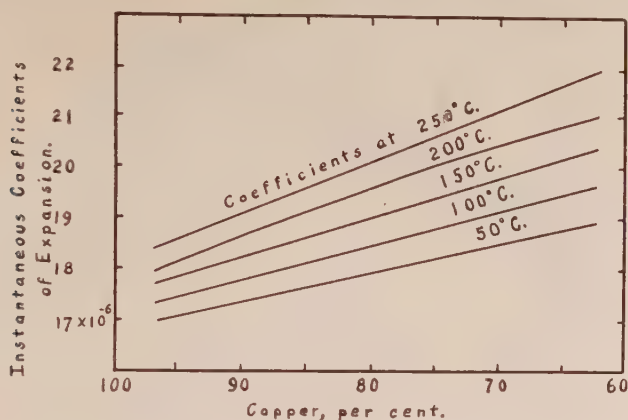


FIG. 3.—RELATION BETWEEN INSTANTANEOUS COEFFICIENTS OF EXPANSION AND COPPER CONTENT OF COLD-ROLLED COPPER-ZINC ALLOYS. (BUR. STDS. *Sci. Paper* 410.)

mens and keep a careful pyrometric control for a period of 30 min. at temperature, the metal being well protected from oxidation. The specimens, with their covering, were quenched in tap water; consequently,

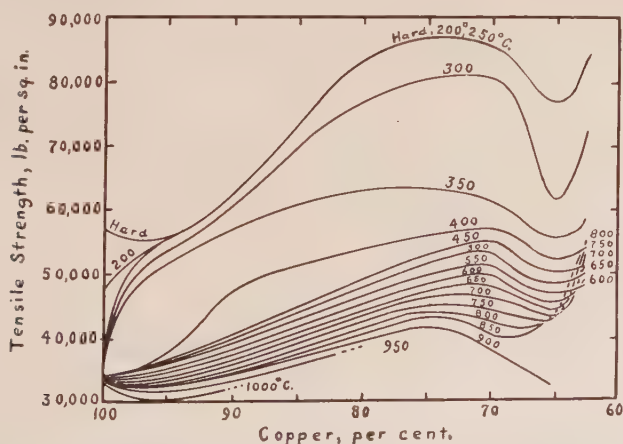


FIG. 4.—TENSILE STRENGTH OF COPPER-ZINC ALLOYS. SHEET, COLD-ROLLED 5 B & S NOS. HARD, AND ANNEALED 30 MIN. AT TEMPERATURES NOTED.

not being in complete equilibrium, most of the specimens from 62 to 67 per cent. copper contained more or less beta, especially those quenched from the higher temperatures.

To be noted in particular are the maximum tensile strength and elongation in those alloys having approximately 72 to 75 per cent. copper.

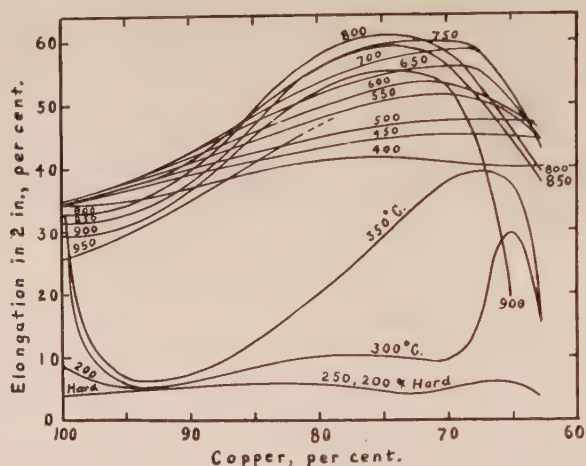


FIG. 5.—PERCENTAGE ELONGATION IN 2 IN. OF COPPER-ZINC ALLOYS. SHEET, COLD-ROLLED 5 B & S NOS. HARD AND ANNEALED 30 MIN. AT TEMPERATURES NOTED.

Again, it will be noted that the elongation of the alloys from 85 to 95 per cent copper is much lower than that of the alloys from 65 to 68 per cent. copper. Finally, the reversal of the tensile-strength curve of the

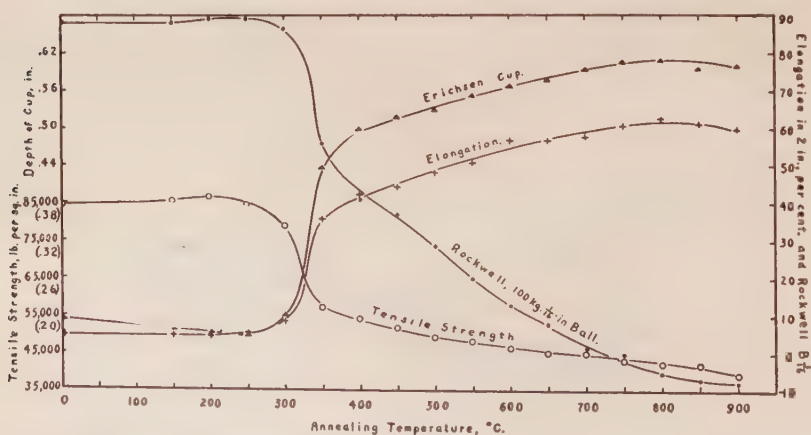


FIG. 6.—ANNEALING SERIES ON 0.040-IN. SHEET BRASS, COPPER 75.43 PER CENT. TEST SPECIMENS, 6 B & S NOS. HARD, WERE ANNEALED 30 MIN. AT TEMPERATURES NOTED AND QUENCHED.

alloys 67 to 62 per cent. copper may be correlated with the position of the α - α + β phase boundary of the copper-zinc equilibrium diagram. Attention is directed to succeeding figures which show maxi-

mum hardness and resistance to fracture by bending in the 75 per cent. copper region, and reversals with the introduction of the beta phase.

TABLE 2.—*Analyses of Sheet Metal Used for Tensile Strength and Per Centage Elongation Determinations*

No. 1	Copper + Silver Per Cent. 99.958			
	Copper Per Cent.	Zinc Per Cent.	Lead Per Cent.	Iron Per Cent.
2	96.83	3.15	0.01	0.01
3	94.83	5.12	.03	.02
4	90.47	9.49	.01	.03
5	85.60	14.35	.01	.04
6	80.80	19.14	.04	.02
7	75.43	24.41	.12	.04
8	72.47	27.47	.02	.04
9	70.14	29.77	.06	.03
10	67.13	32.83	.02	.02
11	65.02	34.80	.15	.03
12	62.37	37.39	.21	.03

ALTERNATE BENDING TESTS

The Landgraf-Turner alternating bending machine is one especially designed and constructed to carry out the Arnold test.⁸ The test is really that of alternate bending beyond the yield point, and the impact of the rocker arm has practically no effect upon the number of cycles required for rupture. The test was conducted by clamping the specimen tightly at the lower end between grooved 1-in. blocks. A rocker arm, having a radius equal to the free length of the test piece, struck the specimen at a point 4 in. above the top of the die block. The rods were bent alternately $\frac{3}{8}$ in. on each side of the vertical position at the rate of 293 alternations per minute. These were recorded by a Veeder counter, which stopped registering when the test piece broke. The specimens were all $\frac{3}{8}$ in. in diameter, and, in preparation for the tests plotted in Fig. 7, were cold drawn from 0.425 to 0.375 in. after a commercial anneal. Six samples of each alloy, 8 in. long, were annealed for 30 min. at temperatures from 200° to 1000° C., or as high as their melting point permitted. The annealed rods were pickled to remove oxides, and were then tested.

It will be seen that this test would have little value as a means of controlling the quality of material purchased in any but this $\frac{3}{8}$ -in. size; consequently, having demonstrated the relative endurance of the copper-zinc alloys under this test, no further work has been done, nor has it

⁸ J. B. Kommers: Repeated Stress Testing—I. An Investigation of a Commercial Endurance Test. Intl. Assoc. Test. Mat. Proc. (1912) 2, Pt. 2, Paper V, 4a.

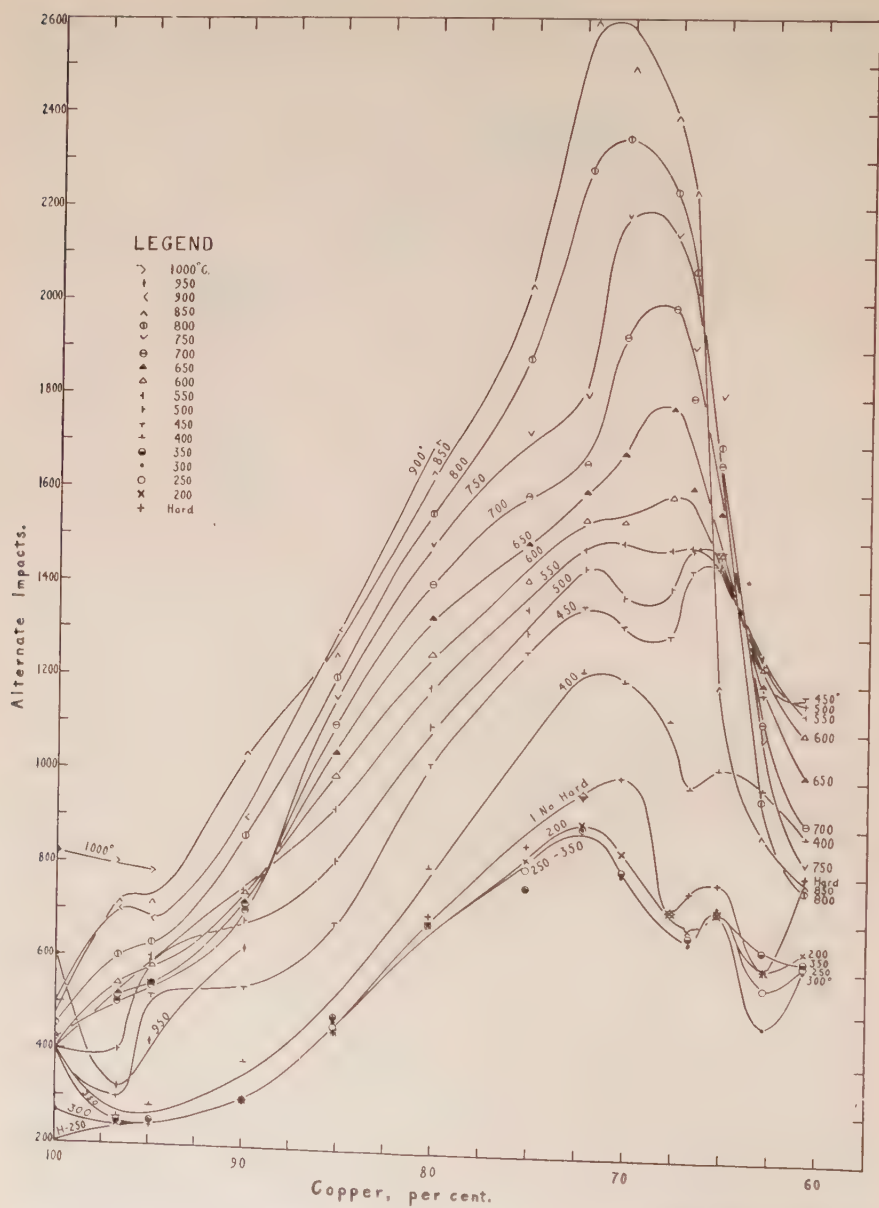


FIG. 7.—RESULTS OF TESTS WITH THE LANDGRAF-TURNER ALTERNATING BENDING MACHINE ON $\frac{3}{8}$ -IN. DIA. RODS COLD DRAWN AND ANNEALED AT THE TEMPERATURES SHOWN.

been deemed essential to our understanding of the physical characteristics of the brasses. The curves in Fig. 7, as has been pointed out, have a striking relation to those of percentage elongation in 2 in. The maximum endurance in general is in the region of 70 per cent. copper, although at anneals from 450° to 650° C. there is a tendency for the maximum to move towards the region of lower copper content. The influence of the beta phase is further shown by the reversals in the relative positions of the plotted points from 65 to 61 per cent. copper. In the region of 90 to 97 per cent. copper there is an unexpected rise in the endurance of the specimens annealed at 1000° C., possibly due to an excessive loss of zinc at the surface while at that temperature.

The analyses of the rods used for the tests are given in Table 3.

TABLE 3.—*Analyses of Rods Used in Alternate Bending Tests*

No. 1	Copper—Conductivity, 100.8; assay, 99.951			
	Copper Per Cent.	Zinc Per Cent.	Lead Per Cent.	Iron Per Cent.
2	96.58	3.37	0.00	0.05
3	94.99	4.99	0.01	0.01
4	89.93	10.02	0.01	0.04
5	85.08	14.87	0.02	0.03
6	80.21	19.71	0.03	0.05
7	75.10	24.85	0.02	0.03
8	72.19	27.76	0.03	0.02
9	70.16	29.81	0.01	0.02
10	67.53	32.43	0.02	0.02
11	66.58	33.22	0.17	0.03
12	65.12	34.70	0.16	0.02
13	62.77	36.99	0.21	0.03
14	60.69	39.27	0.02	0.02

HARDNESS TESTS

Since the introduction of the hardness testing instruments, such as the Shore scleroscope, the Brinell, and the Rockwell tester, all have been used for mill and laboratory control of material. The authors, and others, have in several instances published data on hardness tests of the copper-zinc alloys^{9,10} and have shown the relation of hardness to grain size produced by annealing.¹¹ New data have been assembled in Fig. 8 to show the increase in the hardness of the alloys as the copper content is lowered and as the reduction by cold rolling is increased. The dotted

⁹ C. H. Davis: Testing of Sheet Brass. *Proc. A. S. T. M.* (1917) **17**, Pt. 2, 165.

¹⁰ H. N. Van Deusen, L. I. Shaw and C. H. Davis: Physical Properties and Methods of Tests for Sheet Brass. *A. S. T. M.* (1927) June *Preprint* No. 32.

¹¹ W. H. Bassett and C. H. Davis: A Comparison of Grain-size Measurements and Brinell Hardness of Cartridge Brass. *Trans.* (1919) **60**, 428.

line marked "Annealed" shows, for instance, the approximate hardness of commercially annealed brasses. The curves above show in general the commercial hardness of these alloys after rolling from 1 B & S No. (10.9 per cent. reduction) to 10 B & S Nos. (68.7 per cent. reduction). These curves are assembled from specific data on metal annealed approximately at 600° C., then rolled.

The *actual* range of hardness for these several reductions is, however, quite wide, for it is greatly influenced by the anneal given to the metal before rolling. Consequently, rather wide limits must be allowed,

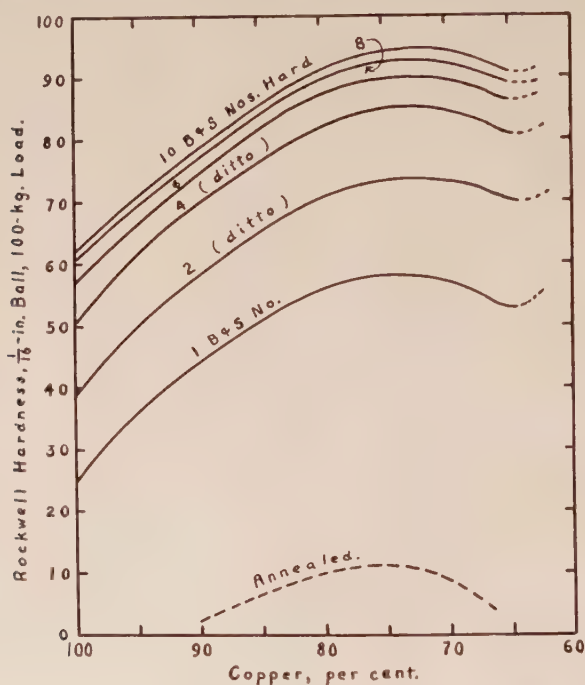


FIG. 8.—ROCKWELL HARDNESS B $\frac{1}{16}$, 100 KG. ON COMMERCIALLY ANNEALED AND ROLLED COPPER-ZINC ALLOYS. THE PRECISE VALUES DEPEND ON THE PREVIOUS ANNEALING TREATMENT.

above and below the lines drawn, to include metal having the reductions shown but having other treatment previous to rolling. In a discussion of Fig. 12, these qualifying factors will again be pointed out. Rockwell hardness tests on annealed sheet metal are shown in Fig. 9, but in this case the 60-kg. load with $\frac{1}{16}$ -in. ball has been employed, for it has been found that the 100-kg. load is too great for the entire field of annealed material.

The maximum point in the hardness curves, both in the cold-rolled and annealed brasses, is at about 75 per cent copper. The rapid increase in the hardness of the annealed specimens from 68 to 62 per cent. copper

is due to the presence of the beta constituent, especially in the anneals from 650° to 850° C. The material used for the tests plotted in Fig. 9 was all in the form of sheet metal 0.040 in. thick, cold rolled 5 B & S Nos.

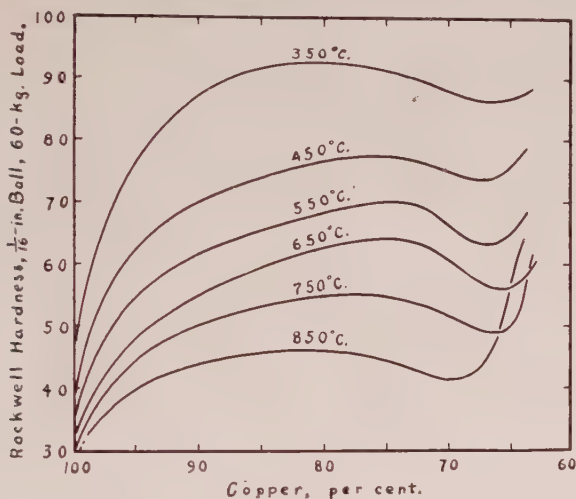


FIG. 9.—ROCKWELL HARDNESS B $\frac{1}{16}$, 60 KG. OF COPPER-ZINC ALLOYS ANNEALED 30 MIN. AT TEMPERATURES NOTED. SHEET METAL 6 B & S NOS. HARD PREVIOUS TO ANNEALING.

hard (44 per cent. reduction) before annealing. Any change in the rolling of the material would have an effect on the ultimate hardness similar to that shown in the paper on grain-size measurements and Brinell hardness.¹²

STRUCTURE AND GRAIN SIZE

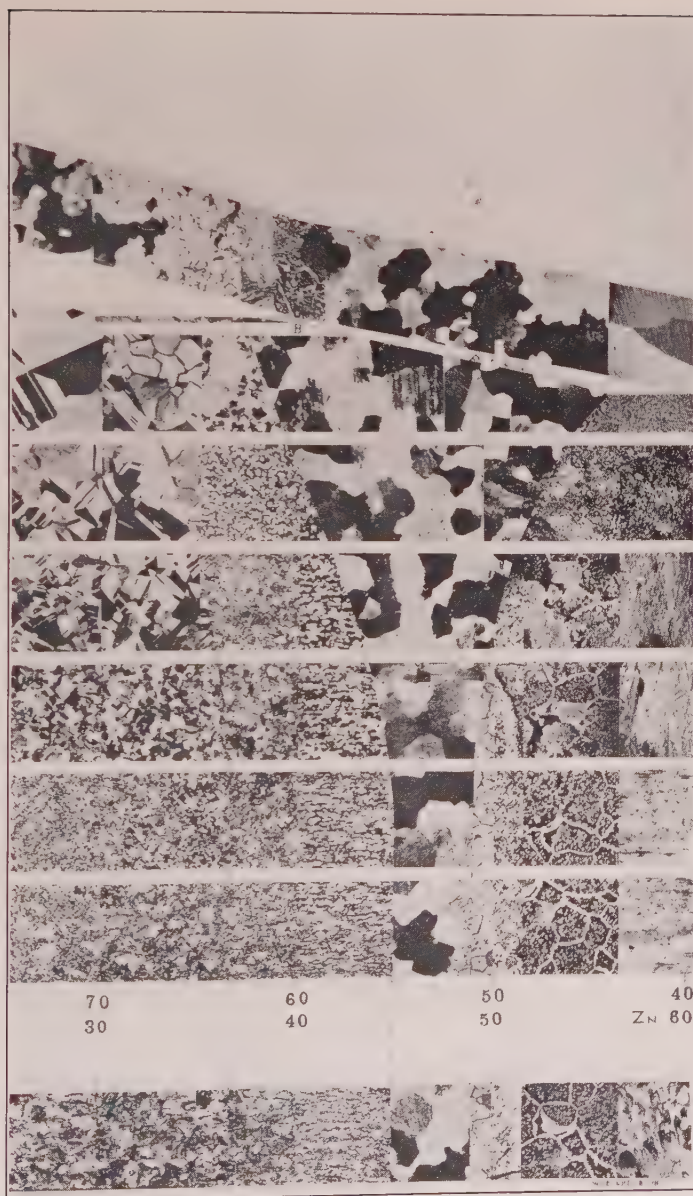
In connection with the determinations of the physical characteristics of the copper-zinc alloys, photomicrographs have been made of all specimens. In order to visualize the changes which take place in the structure during the heat treatment of alloys from 100 to 40 per cent. copper, the photomicrographs on the annealing series have been mounted in the form of the equilibrium diagram as known in 1918. Since then the phase boundary lines have been corrected¹³ but commercially prepared material, not in complete equilibrium, more closely follows the older diagram. In Fig. 10, shown at reduced size, are a large number of squares. These in the original are 2 in. on a side and were magnified 75 dia. The single top row above the liquidus shows the structure of commercially cast bars. The bottom row from 100 to 60 per cent. copper shows the structure after mill treatment by cold rolling and annealing of

¹² See footnote 11.

¹³ M. L. V. Gayler: On the Constitution of the Copper-zinc Alloys Containing 45-65 Per Cent. Copper. *Jnl. Inst. Metals* (1925) **34**, 235.



FIG. 10.—PHOTOMICROGRAPHIC REPRESENTATION OF THE CAST, WROUGHT AND COPPER.) IN THE ORIGINAL THE 2-IN.



ANNEALED STRUCTURES OF ALLOYS OF THE COPPER-ZINC SYSTEM (100 TO 39 PER CENT. ZINC). UNIT SQUARES ARE MAGNIFIED 75 \times

metal finished with a 44 per cent. reduction (5 B & S Nos. hard). It was from such material that the annealing series was made.

The annealing series on pure copper is shown in the single column at the left, while the alloys are shown in the body of the diagram at temperatures from 300° C. to the solidus line. Along the α - $\alpha + \beta$ phase boundary will be noted the separation of β at the boundaries of the α grains; for instance, on the alloy 67 per cent. copper at 850° C. anneal. The pure β phase is represented as being sharply defined. It will be found to shade off into the $\alpha + \beta$ region on the left and

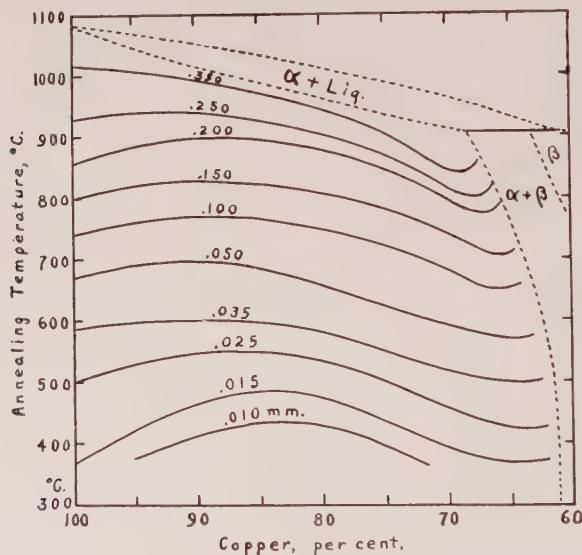


FIG. 11.—GRAIN SIZE OF COPPER-ZINC ALLOYS PRODUCED BY 30 MIN. ANNEALING OF COLD-ROLLED SHEET 5 B & S NOS. HARD.

into the gamma on the right. The β crystal form predominates over both the α and gamma wherever either of these two exist with the β in castings.

It will be seen that the grain size increases with the temperature, but not at the same rate in all alloys. The diameter of average grain of each of these 2-in. squares has been determined by Jeffries' method, and plotted in Fig. 11. The phase boundaries are after Gayler¹⁴ and Genders and Bailey.¹⁵ From a comparison of Fig. 9, showing Rockwell hardness, and Fig. 11, showing grain size, it will be seen that there is a definite relation between grain size and hardness for all of the alloys, but that it is

¹⁴ See footnote 13.

¹⁵ R. Genders and G. L. Bailey: The Alpha-phase Boundary of the Copper-zinc System. *Jnl. Inst. Metals* (1925) **33**, 213.

different in every case. Similar relations will be found between grain size, Brinell and scleroscope hardness.¹⁶

In summary, the structures shown in the body of the diagram are those to be expected following a 30-min. anneal at the temperatures given, on commercially prepared material 5 B & S Nos. hard. The time and temperature of annealing, the hardness and grain size of the cold-rolled metal before annealing, will all have an effect upon the ultimate grain size of the alloys. For discussions of the conditions affecting the grain growth of brasses we would refer to papers by Smith,¹⁷ Upthegrove and Harbert,¹⁸ Phillips and Gerner,¹⁹ Mathewson and Phillips,²⁰ and the authors.¹⁶

The grain size of brass is a condition and a property which is to be faced squarely by all concerned with the drawing and working of the sheet metal. It is recognized that high brass (65 to 67 per cent. copper) will draw more deeply when strongly annealed, for instance to 750° C., but the grain is so large at this temperature that when drawn the articles usually present a rough or "orange peel" surface. A lighter anneal, for instance 600° to 650° C., will allow the metal to be drawn almost as deeply and, at the same time, give a fairly smooth surface. For extra fine finishing, where it is desired to spend little or no work in grinding and polishing, the lighter anneals are to be desired, namely from 425° to 550° C. Such an anneal is also recommended for the drawing of small articles, such as eyelets.

Certain impurities, iron for instance, have a decided effect in lowering the size of grain and in increasing the hardness.

ESSENTIALS OF A SPECIFICATION FOR SHEET BRASS

The tensile-strength determination, after years of study of other methods, remains the fundamental and reference test for sheet brass. No other method of examination of material has been found sufficiently uniform in the results obtained by various laboratories to enable it to replace the tensile-strength determination; yet, on account of the cost and time necessary for the preparation of tensile specimens, ordinary stock and mill control has been based upon hardness tests, such as the Brinell, scleroscope and Rockwell determinations. To show the ductility

¹⁶ See footnote 11.

¹⁷ F. G. Smith: Grain Growth in Alpha Brass. *Trans.* (1920) **64**, 159.

¹⁸ C. Upthegrove and W. G. Harbert: Physical Properties of Cartridge Brass. *Trans.* (1923) **68**, 725.

¹⁹ A. Phillips and G. Gerner: Notes on the Influence of Certain Variables Associated with the Anneal of Cold-worked Alpha Brass. *Chem. & Met. Eng.* (1919) **20**, 622.

²⁰ C. H. Mathewson and A. Phillips: The Recrystallization of Cold-worked Alpha Brass on Annealing. *Trans.* (1916) **54**, 608.

of the sheet metal, the cupping test has been used to supplement the determination of the percentage elongation. On thin metal, especially, the hardness tests alone are inadequate. The microscope may indeed be used to ascertain the hardness or the grain size of the specimens but laboratory practice in making microscopic examinations so often varies that it is desirable to keep in a specification the approximate tensile-strength limits desired. A complete discussion of the problem was presented at the A. S. T. M. meeting in June, 1927.²¹

The question is widely raised as to why the wide limits, allowed in many specifications, must be maintained. There is an unavoidable variation to be expected in rolling and annealing on a commercial scale. The hardness of the finished cold-rolled brass depends on the exact reduction from the previous gage, and also on the grain size of the last

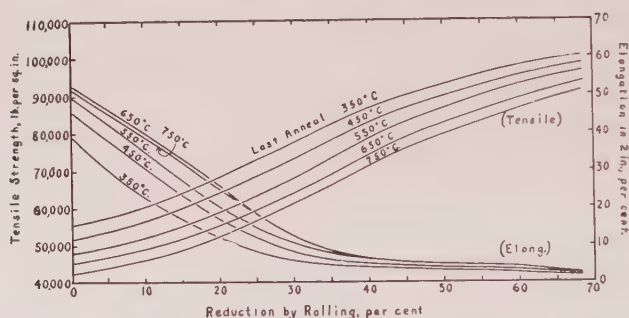


FIG. 12.—BRASS ANNEALING AND ROLLING SERIES, COPPER 67.13 PER CENT., SHOWING EFFECT ON TENSILE PROPERTIES OF THE ANNEAL PREVIOUS TO FINAL ROLLING.

anneal. The variations often tend to neutralize one another, but if they happen to be all positive or all negative the influence on the final hardness is marked. In annealing, although a careful control is maintained, the grain size will depend on the alloy and on the previous grain size, the amount of reduction by rolling, and the time and temperature of annealing. Hence it will be seen that in handling large quantities of metal slight variations in the practice will greatly affect the final hardness or grain size of the brass. In order to illustrate the effect of the last anneal (i. e., the one previous to rolling), on the tensile strength and elongation of cold-rolled brass containing 67.13 per cent. copper, Fig. 12 is presented. Here the tensile strength of the cold-rolled metal, which received a 350° C. anneal before rolling, is decidedly greater than that of the metal rolled following a 450° C. anneal. With higher anneals previous to rolling the tensile strength becomes even lower. The percentage elongation, on the other hand, is higher in the case of the specimens with the higher previous anneal.

²¹ See footnote 10.

In order to make a fair specification for such cold-rolled material, the use to which the metal is to be put must be taken into consideration. Generally speaking, the annealing of brass before final rolling is between 450° and 750° C.; hence, for a given reduction by rolling, tensile tests should fall near, or between, the 450° and 750° C. lines. Fig. 12 shows this relation in the case of one brass only (copper 67.13 per cent.). Each alloy must have its own set of physical-test data from which a specification may then be reasonably prepared. It would be expected that the average tests on mill stock would follow rather closely a median line, but that many isolated tests would approach the upper or the lower boundary lines of the specification. For high brass, such a specification with tensile strength and Rockwell limits has been published jointly with others.²² The standard test procedure is given in appendices 1 and 2 of the same paper.

It has been one of the purposes of this paper to recount the growth of the metallography and methods of test of sheet brass in such a way as to promote a wider knowledge of the subject, and to assist in the preparation of reasonable materials specifications.

DISCUSSION

C. H. DAVIS.—This paper covers in outline approximately 25 years' work of the senior author with his associates on brass and other non-ferrous alloys in that general field, and on the raw materials entering into those alloys. Although copper alone is discussed here, zinc, nickel and other metals were studied.

This brief summary is a compilation of the data on brass most essential to the engineer. Few commercial values are given but plots are arranged in such a way that they may be made of good use, we hope, by engineers. The only material from other sources are Figs. 2 and 3. These were taken from the Bureau of Standards investigation on brass rods prepared under the direction of our laboratory.

W. K. WEBSTER, Bridgeport, Conn.—The metal-using industries in general and this society in particular are to be congratulated that the authors of this paper should have released for publication such a comprehensive assemblage of valuable data. Properly interpreted they furnish the solution for many of the problems encountered in the application of cold-working processes to the entire useful range of copper-zinc alloys. Any invidious criticism ought therefore to be avoided.

It is felt, however, that much added value would have resulted if tables of numerical values of many of the observations had been supplied, as the small scale to which the curves have been plotted permits too large a margin of error in many instances. It is particularly to be regretted that values for the contraction of area have been entirely omitted because, as I have previously pointed out, this property provides a better measure of the ability of a material to withstand cold-working processes than any other.

Attention might well be called on page 69 to the well known phenomenon of differential grain growth due to an annealing operation following an insufficiently severe cold working, since because of the existence of such a situation the annealing practice

²² See footnote 10.

recommended will still produce a rough surface which can only be avoided by increasing the severity of the previous cold working.

The reference to the necessity for what may seem to be unduly wide tolerances is of timely importance, particularly with respect to the effect of concurrent variations of causative factors.

The dissemination of information of this character will also be useful in preventing the imposition of unnecessary or impossible requirements in specifications. Several years ago, during the period when every power engineer with a reputation to sustain felt it incumbent upon himself to add something to the restrictions surrounding the manufacture of condenser tubes, one engineer promulgated a curve the purpose of which was to define the permissible ratio of the maximum to the average dimensions of the crystals comprising the structure of an acceptable tube. According to this curve the maximum permitted ratio was constant for a certain part of the range of sizes allowed and thereafter varied as some function, perhaps a transcendental one, of the size. Investigation showed that ratios twice those permitted represented reasonable though somewhat restrictive values. The publication of such authoritative data as this paper contains will do much to prevent occurrences of this character.

The data presented show the extreme sensitiveness of the various brass alloys to variations in the treatments which are employed in that fabrication.

It is a source of particular regret that the structural diagram was of necessity reduced to such a small scale. Having been privileged to see the original I can testify both to its beauty as a piece of workmanship and the inadequacy of the reproduction. I should also like to express the hope that the authors will at some future date publish a full-scale reproduction of this diagram.

I feel that I cannot let this occasion pass without a tribute of respect for and admiration of the old-time brass makers and the consummate skill with which they carried on a difficult art with nothing but rule of thumb methods for their guidance and yet were able to secure such very excellent material as on the whole they did.

P. D. MERICA, New York, N. Y.—The author pointed out the fact that the elongation in this series of alloys increases with the zinc content together with simultaneous increase in the tensile strength.

I should like to ask whether the reduction of area also increases as the zinc content increases and to the same maximum?

W. H. BASSETT.—It is probably true that the reduction in area does increase as the zinc content increases to the same maximum and follows the elongation. Most of the data given were obtained from testing thin strips and the reduction in area is very difficult and rather uncertain under such conditions. For determining reduction in area it is usual to use fair-sized round rods.

D. K. CRAMPTON, Waterbury, Conn.—In alloys of approximately 70 to 75 per cent. copper there is a better combination of strength and high ductility than is found in the alloys of about 65 or 68 per cent. copper, which are very largely used. This is unquestionably true.

I think the authors used quenched specimens instead of slowly cooled, and I believe if slowly cooled specimens had been used the same phenomenon would have been found but I do not think it would have been as great as is here shown. I would like to ask the authors what their experience has been in that line.

Referring to Fig. 10, which is a composite photomicrograph following the equilibrium diagram, I would like to say that in my opinion this is a very remarkable piece of work. Anybody who has ever tried to make a composite diagram of this kind by fitting pieces together so that they will make a good-looking picture and at the same

time show structural changes will know it must have required a large amount of very careful work.

W. H. BASSETT.—It is probably true that after the appearance of the beta phase quenching does make a difference, but with pure alpha material, so far as we know, there is no difference in physical properties due to quenching. If in the region of the first appearance of the beta phase, slow cooling is resorted to, the beta may revert to alpha, but in mill work the cooling is not usually sufficiently slow to allow much change from beta to alpha to take place. Consequently we feel that quenched specimens in the laboratory more nearly duplicate what happens in the mill.

W. K. WEBSTER.—In this connection, the old brass maker did not know anything about alpha or beta crystals, but it was a very unhealthy activity for anyone to throw a pail of cold water on a pan of hot brass.

Nickel and Monel Metal, with Especial Reference to Annealing

BY C. A. CRAWFORD,* NEW YORK, N. Y.

(Detroit Meeting, September, 1927)

NICKEL and the nickel-copper alloy, the latter generally referred to as monel metal, are available in a variety of wrought and fabricated forms, of which the following are regular commercial products:

Form	Monel Metal	Pure Nickel
Rod.....	Hot-rolled; round, hexagon, square, and flat shapes Cold drawn; round, hexagon, square, and flat shapes Hot-rolled wire rod Cold-drawn wire rod	Same as monel metal
Plates.....	Hot-rolled	Same as monel metal
Sheets.....	Hot-rolled annealed Hot-rolled annealed, pickled Full-finished Full-finished, No. 3 grind one side Full-finished, No. 4 grind one side Cold-rolled (annealed) Cold-rolled, No. 5 polished finish	Same as monel metal
Strip.....	Hot-rolled (flat rods) Cold-rolled (annealed) Cold-rolled (unannealed)	Same as monel metal
Tubes and pipe.....	Gas-welded tube	Seamless tube Seamless tube in I. P. S.
Forgings.....	Bolts, rivets Nuts and washers Forging to order	Same as monel metal
Castings.....	Sand castings Centrifugal castings	Same as monel metal
Electrolytic.....		Cathodes of high purity
Anodes.....		Cast anodes Rolled anodes
Shot and block for melting.	25 to 50-lb. pigs Shot	5, 25 and 50-lb. pigs Shot

* Development and research department, The International Nickel Co.

In an appendix will be found additional details concerning sizes, tolerances, finishes, tempers, applications, etc., of the different groups of wrought products tabulated above.

Chemical Composition

Malleable nickel is produced in a series of grades —A, D, E, and F. Grade A nickel is a low-carbon, pure, malleable nickel. Grade D is a high-manganese nickel alloy containing 4.25 to 5.0 per cent. manganese. Grades E and F are intermediate grades of low-manganese nickel containing 1.75 to 3.0 per cent. manganese.

For melting nickel is produced as shot or blocks in grades F, X and XX. Grade F is primarily intended for the manufacture of nickel cast iron. Grade F nickel is of lower melting point, obtained by alloying, with a small amount of silicon. The X nickel is produced in the form of ingots and shot for melting, and is nickel of high purity. For particular purposes a grade known as XX is supplied, having a minimum nickel content, including cobalt, of 99.40 per cent. nickel.

Monel metal is an alloy of nickel and copper containing approximately 2 parts nickel and 1 part copper. The malleability of this metal is procured through a proper control of carbon, sulfur and silicon content.

Physical Properties

The most interesting physical properties of nickel and monel metal are as follows:

Properties	Monel Metal	A Nickel
Specific gravity.....	8.80	8.84
Weight per cu. in., lb.....	0.318	0.319
Melting point, deg. F. (Ca).....	2400	2640
Coefficient of thermal expansion per deg. C.	25° to 100° C.....	0.000014
	25° to 300° C.....	0.000015
	25° to 600° C.....	0.000016
Thermal conductivity, CGS units.....	0.06	0.14
Specific heat, 20° to 400° C.....	0.127	0.130
Electrical resistivity, ohm-mil-ft.....	256	65
Coefficient of electrical resistance per deg. C.....	0.0019	0.0041
Modulus of elasticity in tension.....	25,000,000	30,000,000
Modulus of elasticity in torsion.....	9,000,000	10,000,000
Endurance limit in alternating stress, lb. per sq. in..	30,000	25,000

Mechanical Properties

In the table below are given typical values for the tensile properties and hardness of monel metal. It should be emphasized that these values are not minimum nor are they specification values. Variations

both above and below these figures are to be expected in normal deliveries of metal.

Forms	Proportional Limit, Lb. per sq. in.	Yield Point, Lb. per sq. in.	Tensile Strength	Elongation	Reduction of Area	Brinell Hardness
Hot-rolled rods.....	35,000	45,000	85,000	40	60	150
Cold-drawn rods.....	60,000	70,000	100,000	20	50	170
Annealed wire, strip or sheet.....		30,000	70,000	Dependent on gage		125
Cold-rolled sheet or cold-drawn wire.....	75,000	100,000	130,000	Dependent on gage		200

The properties of nickel are very similar to those of monel metal with yield point 5000 to 10,000 lb. per sq. in. lower, tensile strength 10,000 lb. per sq. in. lower and Brinell hardness 20 points lower.

WORKING AND FABRICATING OF NICKEL AND MONEL METAL

The working and fabricating of nickel and monel metal are described briefly below, with particular emphasis on features which differ from usual practice for the more common metals, steel or brass. Particular attention is devoted to the annealing of nickel and monel metal since this is an important feature of many sheet-fabricating operations and requires rather special attention. Monel metal and pure nickel may be cast, forged, annealed, pickled, machined, punched, drawn in presses, hand hammered, worked in spinning lathe, soldered, brazed, oxyacetylene welded, arc welded and riveted.

ANNEALING

Interest in the annealing of monel metal and pure nickel centers around sheet and strip or products manufactured from these metals. There are, of course, occasions where it is desired to anneal rod products but these are rare, and practically all forms of the metals except sheet and strip can be purchased in the most suitable temper for the purpose in view and put through manufacturing processes without requiring any annealing. With the sheet and strip forms of monel metal this is not true and a large proportion of the metal purchased is put through manufacturing operations which demand annealing and reannealing in process. The user can buy the material in the most desirable temper for the initial operations but after cold work has been done and the metal hardened, recourse must be had to annealing in order to put the metal in the proper condition to withstand subsequent deformation.

Because general interest in the annealing of monel metal and nickel is concerned primarily with sheet or strip, this paper deals almost wholly

with these forms. Brief mention of the annealing of rods, tubes and forgings is, however, included for reference.

Both monel metal and pure nickel in sheet and strip form are influenced as to ductility by the same conditions in the same way and respond in general alike to the same treatments. Since like principles appear to govern the development of maximum ductility for these two metals, they can in nearly all cases be treated by identical methods. Monel metal and pure nickel cannot be hardened by any heat-treatment or quenching process but can be softened (annealed) by slow heating and cooling.

Furnace Refining of the Metals

Associated with the effect of annealing upon the ductility of these metals are a number of influences not wholly dependent on the heat treatment. Such influences are the character of the metal surface, the previous treatment of the metal with reference to cold work, the grain size of the metal when presented for annealing, the composition and furnace refining of the metal.

Skillfully controlled furnace and pouring practice are maintained so that the composition of the metal conforms to prescribed narrow limits with reference to those elements which are of the nature of impurities or are residuals from deoxidation equilibria. The carbon, sulfur and silicon must be and are readily held within specified limits. The variation in analysis of these elements as found in the commercial products has been shown to be too small to exert any influence on ductility. Exhaustive determinations on regular daily production of the mill indicate that within limits of variation throughout the range in which the commercial products fall, the iron or the manganese content does not show any consistent effect in increasing or decreasing the ductility of the metals.

Surface Effect

One very definite influence upon the ductility of monel metal and pure nickel sheets and strip is the character of the surface. It has been convincingly demonstrated by repeated tests that any reduction of ductility of the surface will enormously reduce the ductility of the whole section. If the surface carries oxide, however thin, or reduced oxide, or porosity arising through mechanical abuse (tool scratching, guide marking, seams, laps, blisters) or through chemical attack or corrosion, the ductility of the sheet will be definitely lowered. Conversely, if such weakened surface can be removed as by polishing or pickling, the test pieces from the same sheet will show increases in ductility of 10 to 15 per cent. or more (which may mean the difference between success or failure in fabricating operations).

Cold Work Before Annealing

The amount of cold work done before annealing has a definite and constant influence upon the ductility of these metals after annealing. If only a very small amount of cold work is done (for example, 10 per cent. reduction by cold rolling) the full ductility cannot be restored by any method of annealing. A study of the cold working of monel metal has led to the conclusion that because of this fact it is definitely detrimental to carry out a series of cold-working and annealing operations on monel metal and nickel in which the amount of cold working between one annealing and the next is less than 20 per cent.

On the other hand, if the cold working is carried too far it is extremely difficult to restore full ductility without danger of overannealing, which would show up in coarse grain size and embrittlement. Excessive cold work under extreme conditions may even produce internal fractures which cannot be healed, and which will result in the straight line type of hard fracture that develops with seasoning, and has been described by the terms "season cracking" or "corrosion cracking." The relation between annealing of monel metal and nickel and the amount of cold work preceding annealing is illustrated by the graphs in Fig. 1. These show that 20 to 25 per cent. of cold work before annealing gives the best result in ductility, softness and grain refinement. Accordingly, it is best to lay out all cold-forming operations, as, for example, in draw press work or die work of any sort, so that the amount of cold work between one annealing and the next will be at least 20 per cent. and not over 30 per cent., measured as reduction of diameter of the shape or section.

Box Annealing Temperatures

Figs. 1 and 2 show the limits of time and temperature which produce the best results on ductility for relatively slow (long-time) annealing. These limits refer, of course, to enclosed or "box" annealing, as it must be clear that such extended annealing intervals are uncalled for except where the product is annealed inside a box. Open annealing takes much less time and is dealt with in a later paragraph. A study of the curves shows that the most reliable results are had in temperatures in the vicinity of 1400° F. for a relatively long heating time.

Heating at 1200° F. for reasonably short times fails to produce either softness, ductility or grain refinement, although if it is practical to allow for annealing as long as 12 to 14 hr. at heat, and under carefully controlled temperature limits, ductility will finally be developed at 1200° F. This is indicated in Fig. 3.

Annealing at 1600° F. will give excellent ductility in a shorter time interval, but is accompanied by considerable danger of grain growth and

consequent loss of good drawing ductility. If the temperature can be accurately controlled and the time at heat limited without any chance of overrunning the allotted interval, 1600° F. can be used and will get the work out in less time.

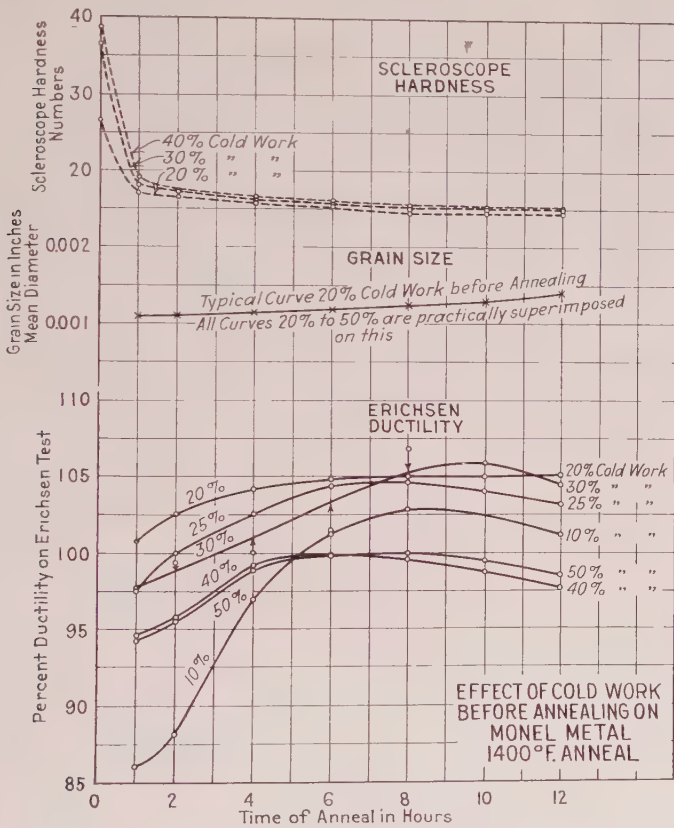


FIG. 1.—EFFECT OF COLD WORK BEFORE ANNEALING ON MONEL METAL; 1400° F. ANNEAL.¹

One-thousand eight hundred degrees Fahrenheit is clearly too high a temperature for box-annealing monel metal and nickel, and will surely result in the development of coarse grain and loss of ductility. Softness will of course be produced by the high temperature.

¹ The data upon which the graphs in Figs. 1, 2 and 3 are based, are typical only and, in the instance of each figure, represent values obtained on one typical heat. Variations will of course be found in normal deliveries. The graphs are based in part upon data obtained by Dr. W. A. Mudge, metallurgist, Huntington Works, The International Nickel Co.

Time of Box Annealing

As shown in Fig. 1, at 1400° F. the time of annealing at temperature required to develop full ductility and softness is from 4 to 8 hr. This time interval is also the best for material which has been cold worked 25, 30, 35 and 40 per cent., based on data for other curves not included in this paper.

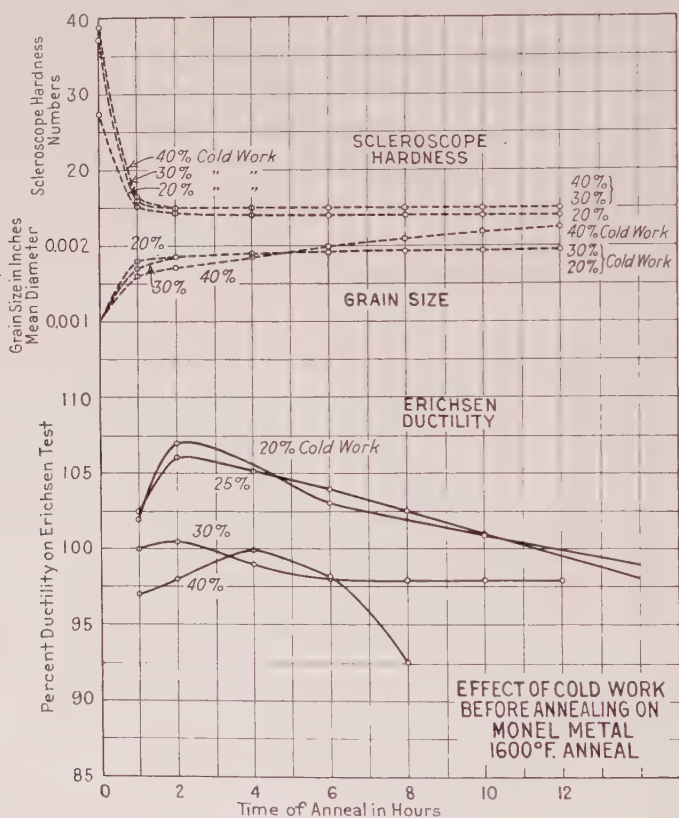


FIG. 2.—EFFECT OF COLD WORK BEFORE ANNEALING ON MONEL METAL; 1600° F. ANNEAL.²

At 1600° F. the time must be materially reduced. Annealing is completed in from 1 to 2 hr. in every case and is so well advanced after 1 hr. that as a guide to good practice 1 hr. should be considered the annealing interval for high temperature (1600° F.) box annealing. Where time is an important factor, as it often is in plant production, very good results can be had under these conditions, but the temperature control must be particularly careful, and elaborate precautions arranged so that the time of heating will not be excessive. One hour at 1550° to 1650° F. should be the rule followed.

² See foot note No. 1.

If time is not a consideration and particularly accurate furnace temperature control is available, monel metal and nickel will anneal to practically full ductility and softness at 1200° F. after 12 to 14 hr. at temperature. Under these conditions the grain growth will be a minimum and the final grain size will be smaller than can be maintained by the 1400° or 1600° F. annealings described above.

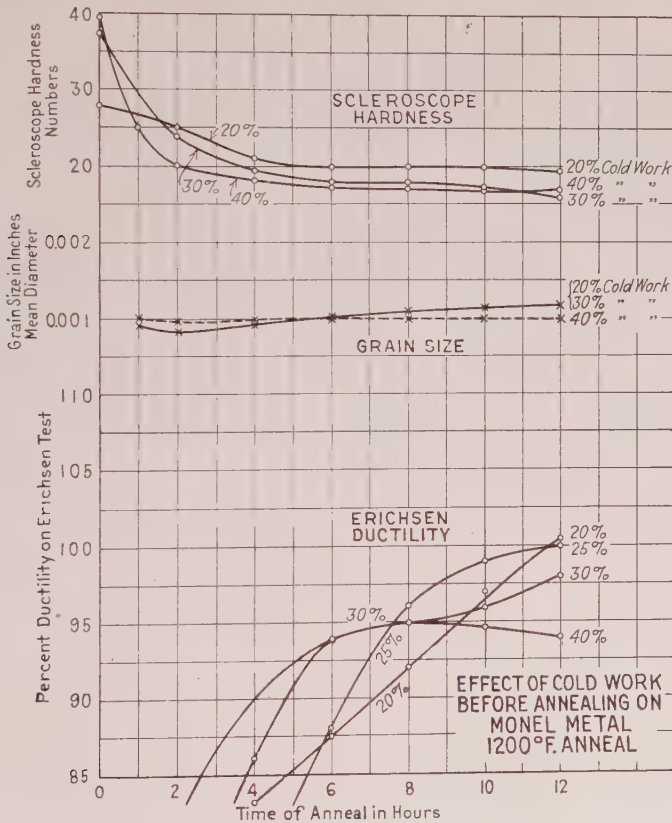


FIG. 3.—EFFECT OF COLD WORK BEFORE ANNEALING ON MONEL METAL; 1200° F. ANNEAL.³

Grain Size

The ductility of monel metal and nickel sheets and strip has a direct relation to the grain size. As the grain size increases the ductility for drawing operations will decrease, even though the metal may be softer. Grain size also has an important bearing on the value of finished products. Coarse grain material may sometimes be successfully put through cold-drawing operations, but will develop the so-called pebbled or orange peel surface through cold deformation. Such a pebbled surface will

³ See foot note No. 1.

spoil the appearance of the finished article and also, through presenting a comparatively coarse surface, reduce the value of the metal to resist corrosive influences. If the article is to be polished, any tendency to develop a pebbled surface must be eliminated, as it is practically impossible to polish coarse grain metal and certainly not at economical costs.



FIG. 4.—TYPICAL FINE, MEDIUM AND COARSE GRAIN IN MONEL METAL. $\times 100$.

Fine-grained monel metal and nickel means metal whose grains will measure an average diameter of 0.0010 in. Medium-grained metal is that whose grain size measures from 0.0015 to 0.0017 in. Any metal having grains whose average diameter is greater than 0.0020 in. is considered coarse grained. This is illustrated in Fig. 4.

Gas Annealing

In box annealing an embrittlement of the metal will sometimes occur due to leakage of air or furnace gases into the annealing boxes. One good way of preventing this is to introduce gas inside the boxes during annealing and cooling. Natural gas is best for this purpose but city gas scrubbed free of sulfur compounds will also serve. The practice is to insert a bent pipe through the sand seal and under the annealing cover, or into a tapped hole in the cover or pan. The pipe should be approximately $\frac{1}{2}$ in. iron pipe size and should extend from the box under the furnace door and a little way outside. The outside end of the pipe is connected to a source of gas with a flexible connection.

All air inside the box should be swept out with gas to prevent explosions and the gas pressure then reduced to a very gentle flow so that the gas will burn with short flames through the sand seal or at any small leaks in the cover. Very little gas is required during the heating but it

should be turned up to keep small flames on the box as soon as firing is stopped and the soaking at heat begun, followed by cooling. Gas should be kept on the box until the product has cooled below 300° F. This method of annealing will give a deoxidized surface, which can be delivered to the next cold-forming operation directly or given a short acid pickle.

Open Annealing

Excellent results in restoring ductility of monel metal and nickel after cold working are given by open-annealing methods. The principal objection to the universal adoption of open methods for handling the annealing of these metals is the difficulty in preventing surface oxidation or of removing such oxidation if it is permitted to form. Furnaces are available in which monel metal and nickel sheets are being annealed and cooled in a non-oxidizing atmosphere which results in a bright, practically oxide-free surface. Furnaces of this type are not, however, common equipment and are expensive to install. Where any continual large production work on these metals is contemplated it will certainly be worth while to install a furnace of this type and open anneal all monel metal and nickel products.

If these metals are to be annealed in an open furnace under an oxidizing atmosphere, measures must be taken to remove the oxide surface before any further cold work is done, or otherwise a large proportion of the ductility of the metal will be lost. In following this practice with other metals it is natural to think of pickling after annealing as the simplest solution. This can be done, but requires solutions which are extremely corrosive and disagreeable to handle and also requires a long time. Monel metal and nickel can be pickled in a solution of nitric and sulfuric acid at practically boiling temperature. The solution is hard to hold in any vessel and fumes extensively. For the best results, a pickling operation should be used none the less, and this can be done by careful planning for ventilation. The recommended pickling solution is made up of $1\frac{1}{8}$ lb. sodium nitrate added to a mixture of $\frac{3}{8}$ gal. 60° sulfuric acid in 10 gal. water. During pickling the temperature must be kept at 185° to 190° F. Another precaution is the necessity of cleaning away all grease before pickling, as otherwise the acid cannot reach the metal surface.

Open-annealing Conditions

For open annealing monel metal and pure nickel the products should be heated rapidly up to 1650° to 1750° F. and held at that temperature for 5 to 7 min. The time should not be permitted to exceed 15 min. This practice will give full ductility and will preserve a fine grain size in the metal. It will not, however, give quite as soft a sheet as the box-annealing practice.

Alcohol-quench Anneal

A method of reducing, or partly reducing, the surface oxide that results from open annealing is the use of an alcohol quench after annealing.

To carry out this method the open-annealing practice given in the preceding paragraph should be followed, and the products heated in a sulfur-free furnace atmosphere to a temperature in the range of 1650° to 1750° F. for 5 to 15 min. The products are then withdrawn and quickly plunged into a quenching mixture of alcohol and water. Handling must be arranged so that the article will enter the alcohol-water solution at a bright yellow heat. Allow the article to cool a few minutes in the quenching bath and it is then ready for further cold working.

The alcohol-quench anneal when skillfully carried out will leave a clean white surface on nickel. When applied to monel metal the surface will take on a copper color. The flash of copper is extremely thin. The metal is softened so that it can be redrawn in presses or reworked cold by spinning or hammering. For best results, however, and to take advantage of the full ductility of the metal, it is advisable to introduce a pickling operation after the annealing. The pickling practice has been briefly described above. The alcohol and water-quenching solution referred to is a mixture of 1 part wood (methyl) alcohol in 80 parts water. Denatured grain alcohol is not as effective as wood alcohol in the process.

Annealing of Rods and Other Products

The annealing of monel metal or pure nickel rods, tubes, etc., is not often necessary and where needed a small amount of surface oxidation does not matter. The best method is to heat the rods directly in a sulfur-free furnace atmosphere to temperatures between 1650° and 1750° F. for approximately 15 min. after the rods or tubes come up to temperature. The products can then be cooled in the furnace or withdrawn into the air. The alcohol-quench annealing method can also be used. If it is necessary to anneal monel metal or nickel rods without oxidizing the surface, they may be gas-annealed in a large steel pipe closed at both ends with the introduction of gas as described above.

SUMMARY OF ANNEALING PRACTICE

Monel metal and nickel may be box-annealed or open-annealed.⁴ In box-annealing care must be used to keep tight seals and avoid leaks into the box.

Charcoal inside the annealing box is beneficial.

⁴The notes are given briefly to serve as guides to experienced annealers.

The charge should be kept out of contact with iron, steel or sand in the annealing box.

Box-annealing with gas introduced to maintain a deoxidized surface is fully practical with both monel metal and nickel.

Monel metals and nickel may be open-annealed under very slightly oxidizing conditions as in muffles or enameling kilns.

In open-annealing it is good practice to quench in a 1-to-80 mixture of methyl alcohol and water to reduce oxides on the surface. The quenching does not harden the metal.

Temperatures for box annealing are 1400° to 1500° F. and for open-annealing 1650° to 1750° F.

Time for box-annealing is 4 to 8 hr. at 1400° F.; or 1 hr. at 1600° F.

Open-annealing is completed in 5 to 7 min. at temperature.

CASTING

Some special experience is necessary for making good castings in monel metal and nickel because of their high melting point, and the necessity for care in control of sulfur, silicon and carbon. Printed instructions on casting and methods are available to operators.

FORGING

Monel metal and nickel are easily forged after brief experience. Certain care is necessary to maintain favorable heating conditions and temperatures. The essential requirements are:

1. Low-sulfur fuel; natural gas, retort gas, fuel oil, (low-sulfur) producer gas. Coal is not recommended for heating except for muffle furnaces.

2. Complete combustion outside the hearth; an outside combustion chamber or premixing burner should be employed. A rash flame impinging on the work should be avoided.

3. Maintenance of fuel-air balance; hearth atmosphere should be held very slightly on the oxidizing side of neutral.

4. Proper working temperatures; for monel metal forging should be done at between 1850° and 2100° F., bending between 1850° and 1950° F. For nickel forging should be done at between 1850° and 2200° F. No forging should be done on either metal at red heat below 1800° F., nor should they be allowed to bend in the red range.

Monel metal and nickel may be forged in dies under hammers but not in presses. More power and heavier forces are needed for forging monel metal and nickel than for steel of the same size section. Forging instructions in considerable detail are supplied by the manufacturers of these metals.

PICKLING

Monel metal and nickel can be pickled in very hot solutions of sodium nitrate, sulfuric acid and salt. The manufacturer should be consulted in this, as the solutions work quite slowly and are unpleasant to handle.

MACHINING

Monel and nickel may be machined without difficulty. Cold-drawn material machines more easily than softer (hot-rolled or annealed) products.

Generous lubrication is generally essential in machining monel metal and nickel but they are often machined successfully without lubricant. Tools for machining should be ground with a sharp cutting angle—considerable hook or rake. Production should be about two-thirds that of machinery steel for the same piece.

PUNCHING

Monel metal and pure nickel may be punched up to practically the same limits as for steel, but greater power will be required.

PRESS DRAWING

Monel metal and pure nickel may be easily worked in drawing presses. Ordinarily these metals can be drawn into deeper shapes without annealing than is possible with cold-rolled steel.

Die clearances should be ample, a little greater for monel metal and nickel than for steel. Drawing dies should be of very hard steel or iron or else of hard bronze (20 per cent. tin, 80 copper). Soft steel dies are galled or scored by monel metal and nickel. Dies should be laid out for reduction from the blank of 30 to 35 per cent., followed by 30 per cent., 25 per cent., 20 per cent., etc. Wall thickness can be reduced on a die and mandrel designed for the purpose.

Annealing should be done after second and subsequent draws.

Lubricants that wet the metal should be used. Heavy lubricants are ordinarily best.

HAND HAMMERING

Monel metal and nickel can be hand-hammered and coppersmithed within limits. Frequent annealing is necessary as the metal hardens rapidly. It is very difficult to "raise" the metal by "bumping," but this can be done in a limited way by skilled workmen.

SPINNING

Monel metal and nickel may be spun within limits; nickel is easier to spin than monel metal. The metals harden rapidly under cold work and

should be frequently annealed. Spinning should be done as rapidly as possible, avoiding reworking the same metal excessively.

SOLDERING

Monel metal and nickel are easily soldered. Good preliminary cleaning by scraping, grinding or with nitric acid is necessary. Flux with a good grade of zinc chloride flux.

In using a soldering iron, work slowly to allow heat to penetrate the work so that the solder will run freely. Hold the work with clamps to prevent springing before the solder has hardened.

BRAZING

Monel metal and nickel may be joined by brazing with brass, nickel silver, or silver solder. Ordinary brazing methods are followed. Use a flux of 1 to 1 borax and boric acid.

OXYACETYLENE WELDING

Monel metal and nickel may be welded with oxyacetylene torch after a little experience. The flame should be very close to neutral on the reducing side and the work should be welded rapidly and not reworked. The metal to be welded should be clamped so that it can not move while or immediately after the welding is done. A flux of 1 to 1 borax and boric acid is used.

The art of acetylene-welding these metals is not a simple one to master. The manufacturer of the metals should be consulted for further detail and instruction.

ELECTRIC WELDING

These metals may be welded by electric arc, using a deoxidizing flux and with reversed polarity. This art is not simple to master and the manufacturer of the metals should be consulted.

RIVETING

There is nothing unusual about riveting monel metal and nickel. In general, they should be riveted cold.

APPENDIX

DETAILS REGARDING THE DIFFERENT CLASSES OF COMMERCIAL NICKEL AND MONEL METAL PRODUCTS

HOT-ROLLED RODS

Monel metal and pure nickel are manufactured in the form of hot-rolled rods in all commercial sizes from $\frac{7}{32}$ to 6 in. In sizes from 4 to 6 in. the rods are supplied

either rolled or hammer-forged and in both cases are rough turned. Larger sizes than 6 in. can be supplied to order in hammer-forged rough-turned rods.

The rods are ordinarily supplied in mill lengths of from 5 to 20 feet.

Hexagon, square and flat sections are regular products. Special sections are rolled to order.

The hot-rolled rods in straight lengths are of ordinary commercial straightness. In sizes of $\frac{5}{8}$ in. dia. and smaller the rod can be supplied in coils.

The size tolerance is governed by the standards applied to steel of the same section. Where hot-rolled monel metal rods are to be machined, an allowance is necessary to clean up on all guide marks, etc., in the surface. For rods less than 1 in. allow $\frac{1}{8}$ in. on diameter; for rods 1 to 2 in. allow $\frac{3}{16}$ in.; for rods 2 to 3 in. allow $\frac{5}{16}$ in.; for rods 3 in. and larger allow $\frac{3}{8}$ in. on diameter.

Hot-rolled rods may be machined; they may be bent cold or cold upset; they may be forged hot; they may be joined by riveting or by welding—either electric or oxy-acetylene. Hot-rolled rods are used in the sizes as rolled, after minor machining operations, or after forging.

COLD-DRAWN RODS

Cold-drawn rods are supplied in all sizes of rounds from $\frac{1}{2}$ to 3 in. and also in some square, hexagon and flat sections and in special cold drawn shapes to order. Ordinary cold-drawn rods will come within the following tolerance limits:

Size..... Plus 0.000 in., minus 0.002 to 0.005 in.

Straightness.... $\frac{3}{16}$ in. on random mill lengths.

Especially straight cold-drawn rods are supplied under the designation "pump rods." These have a straightness tolerance of 0.005 to 0.008 in., depending upon the size of rod, in 42 in. length. Extra close size tolerances can be maintained on special orders and at extra cost.

Cold-drawn rods are ordinarily supplied unannealed. They can also be supplied stress-relief annealed, or full-annealed. Full hard rods can be procured in the smaller sizes, beginning with the wire sizes.

Cold-drawn monel metal or pure nickel is ordinarily selected where it is desired to take advantage of the considerably increased tensile strength and yield point that are the result of cold drawing. Where high yield point is the governing consideration, stress-relief annealing should also be specified.

Cold-drawn monel metal or pure nickel is used where accuracy to size is the governing consideration, as in pump rods, rotating shafts, etc.

Cold-drawn rods are used for parts to be machined. For three reasons cold-drawn is to be preferred for this purpose to the hot-rolled product: (1) Freer machining quality at medium hard temper in these metals, (2) accuracy to size for passing collets, and (3) freedom from surface blemishes. For full automatic and hand-screw machine work, cold-drawn rods should always be used, and often for ordinary machining operations where the volume of metal to be removed is large in proportion to the total volume of metal in the piece handled (see above, under machining).

Cold-drawn rods may be used where appearance is a consideration; in monel metal and pure nickel they are bright, permanently white, non-rusting, practically non-tarnishing and readily polished.

Cold-drawn monel metal and nickel rods are used for forgings where the quality of the surface of the finished forging is of importance, or where surface seams must be avoided. An example of this is found in the manufacture of turbine blading, balls for check valves, etc.

Cold-drawn monel metal and nickel can be bent cold, upset cold, or drawn cold, hot-forged, machined, welded, brazed or soldered.

WIRE ROD

Monel metal and nickel wire rod is hot-rolled rod of small diameter ($\frac{7}{32}$ to $\frac{5}{8}$ in.) supplied in coils. The size and roundness tolerances are governed by standards applied to steel. Wire rod is ordinarily supplied as coiled hot in the rod mill; it also can be supplied, on order, annealed or pickled.

Wire rod is used for redrawing into wire or for the manufacture of bolts, nuts or similar items in upsetting machines.

The hot-rolled monel metal and nickel wire rod can be bent cold, forged or welded. For cold upsetting, cold-drawn annealed wire is superior to the hot-rolled product.

COLD-DRAWN WIRE

Monel metal and nickel wire can be supplied in all sizes down to 0.001 in. The size tolerances are governed by the requirements of the customer and ordinary commercial standards.

Monel metal and nickel wire can be supplied in various tempers, ranging from dead soft to full hard or spring temper. The dead soft and soft tempers are bright annealed, and the intermediate and hard tempers carry a bright finish resulting from the drawing dies.

Monel metal and nickel wire are used for cold upsetting and rolled threading operations, for which purpose $\frac{1}{4}$ hard temper is suitable. Wire is used extensively for small automatic screw machine products. Half-hard temper material is most suitable for this purpose.

Monel metal and nickel wire are used for welding rod in the full annealed condition.

Monel metal and nickel wire are used for springs to work under corrosive conditions. For this purpose full hard or spring temper material is supplied, having a minimum tensile strength of 135,000 lb. per sq. in.

Monel metal and nickel wire are used extensively for weaving into filter cloth and screens.

PLATES

Hot-rolled plate in monel metal and pure nickel are produced in thicknesses from $\frac{1}{4}$ in. to 1 in., in widths up to 90 in. for all but the heavier gages, and in long lengths, maximum at 240 in. for $\frac{3}{8}$ thickness. There are slightly shorter limits of length on lighter and heavier plates. These plates are not annealed or pickled and carry an oxide surface.

Plates can be supplied sheared to circular form or to template.

Dished and flanged heads are available in $\frac{1}{4}$ to $\frac{1}{2}$ in. gage; 12 to 60 in. outside dia. and $2\frac{1}{2}$ in. maximum depth of flange.

Monel metal and pure nickel hot-rolled plates may be bent hot or cold on a radius as much as or more than the thickness of the plate. They may be welded or riveted.

HOT-ROLLED SHEETS

Monel metal and pure nickel hot-rolled sheets, as the name implies, are produced by a hot-rolling process similar to that used for sheet steel, and are finished by annealing and resquaring. The surface of the sheets is not refined in any way. These sheets are produced in U. S. standard gages from No. 26 (0.018 in.) to No. 3 (0.250 in.). The maximum width is greater for the heavier gages. For intermediate gages, sheets up to 50 in. wide are produced. The maximum length depends upon the gage and width, and goes as high as 156 in. for sheets 0.050 to 0.125 by 48 in. wide. In widths up to 44 in., 0.050 to 0.125 in. thick, the maximum length is 172 inches.

The hot-rolled monel metal and nickel sheets are intended for mechanical purposes where surface appearance is not a determining factor. These sheets can be used for architectural purposes, as on roofs, for gutters or flashings, and for engineering constructions such as drying apparatus.

The hot-rolled monel metal and nickel sheets may be bent on a radius not less than the thickness of the sheet; they may be riveted or welded. With extra preparation in cleaning or pickling the surface areas to be worked, these sheets may also be brazed or soldered. They are not suitable for cold drawing or spinning, nor are they intended for lock-seaming.

FULL-FINISHED SHEETS

These sheets are produced by methods similar to the full-finished steel sheets of the automobile body or panel stock class. They are hot rolled, annealed and pickled, cold rolled lightly (2 to 3 per cent. cold reduction), reannealed, leveled and resquared.

Full-finished sheets are produced in the same sizes as the hot-rolled sheets, from 0.018 to 0.250 in. in thickness; width limits of 40, 44, 48 or 50 in., depending on the gage and length. They are reasonably flat and free from buckles, and are produced in one temper only, which is a soft temper. They are supplied with ground finish of two grades. (For detail see under polished sheets.)

Full-finished sheets are the most widely used sheets for general purposes, and are the standard commercial monel metal or nickel sheets. These are used for all sorts of architectural cabinet work such as counters for hotels and restaurants, hospital tables, laundry and textile machinery. They are selected for all sorts of sheet metal work where appearance is a major consideration, and where it is desired to grind or polish a finished fabricated article. They are also used to meet corrosive conditions which are severe enough to require a smooth surface.

Full-finished monel metal and nickel sheets may be lock-seamed both across and along the grain; joined by riveting, and welded, brazed and soldered.

Full-finished sheets are not the best product for severe cold-working operations, such as deep drawing in presses or spinning. Cold-rolled sheet or strip is better for such purposes. For simple, relatively shallow, drawing-press operations the full-finished sheets will sometimes serve. They should not be chosen for cold-forming operations until after practical trial in each new case.

COLD-ROLLED SHEETS

Monel metal and nickel cold-rolled sheets are produced by a rolling practice especially adapted to the purpose. These sheets are hot rolled, annealed and pickled and finished by heavy cold rolling, leveling, reannealing and resquaring. They are produced in thicknesses of from 0.018 to 0.250 in., in widths up to 36 in. and lengths up to 166 in. depending on the gage. The gage tolerances on these sheets can be closely controlled. These sheets are flat.

The cold-rolled monel metal sheets can be produced in a range of tempers from soft to hard measuring the hardness in a range between 16 and 40 Shore hardness. On cold-rolled sheets harder than one-quarter hard flatness must be sacrificed. The standard cold-rolled sheet is of soft temper, and any other tempers are produced only on order.

The cold-rolled monel metal and nickel sheets carry a highly refined surface, free from all except the smallest blemishes. They are used where appearance is a consideration, surface imperfections are undesirable, or the finished product is to be buffed to a high polish, and under most severe corrosive conditions where a smooth surface will improve the resistance, or where the highest ductility is required.

Cold-rolled monel metal or nickel sheets are specified for all cold-forming operations in presses. Cold-rolled sheets are used for hand forming work such as coppersmithing or spinning. Cold-rolled sheets in soft temper may be lock-seamed along and across the grain. They may be cold worked in a drawing press into the most difficult shapes, they may be formed by spinning, within limits, they may be riveted, welded, brazed or soldered.

POLISHED FULL-FINISHED SHEETS

Depending on the gage full-finished sheets in thicknesses from 0.021 to 0.250 in., in widths up to 48 in. and lengths up to the limits of the sheet schedule can be supplied in two grades of ground finish. These finishes are ordinarily supplied on one side only, but can be supplied on two sides of the sheets.

The first finish is specified as No. 3 grind, which is a fine emery finish, in appearance like the effect of a coarse wire brush. A higher grade of finish is known as No. 4 grind and is produced by carrying the polishing on to the finest grades of emery. This is a very fine satin finish of uniform appearance with a good medium lustre. Both the No. 3 and No. 4 grind show a wavy effect which improves the uniformity of the appearance in the finished product.

The No. 3 finish, which is supplied at a lower price, is usually used as received, for counter work such as hotel or restaurant cabinets, trim, etc.

The No. 4 finish is usually selected where a finer appearance is desired or where it is intended to further polish and buff the finished product. The No. 4 finish is suitable for trim, moldings and the highest grade of cabinet work.

The physical properties of the ground finish sheets, both No. 3 and No. 4 grind, are the same as for the full-finished, hot-rolled sheets, and they may be adapted to the same purposes and worked up to similar limits with reference to bending or forming.

COLD-ROLLED POLISHED SHEETS

Cold-rolled monel metal and nickel sheets are supplied in No. 5 finish, which is a high polish produced by buffing. These sheets are supplied in gages from 0.021 up to 0.062 in. in widths up to 36 in. and lengths up to the limits of the sheet schedule. The finish on these sheets is a straight buff which brings out a high luster. Sheets are designed for the highest grade of cabinet work or for the fabrication of articles which must be finished to a high lustre.

The properties of these sheets are the same as for the cold-rolled sheets and they may be subjected to similar forming operations. It would not, however, often be desirable to employ polished sheets for severe cold forming because the polish would be destroyed and a regular cold-rolled sheet would serve as well.

HOT-ROLLED STRIP

Hot-rolled strip is produced in monel metal and pure nickel. This is in effect a wide flat rod, and the comments under the heading of "Hot-rolled Rods" apply here. The hot-rolled strip is ordinarily supplied in mill lengths of from 5 to 20 ft. Thicknesses from $\frac{1}{8}$ to $\frac{5}{8}$ in. are supplied in widths up to the limit of the mill. The maximum width varies with the thickness. Strip under 0.250 in. in thickness is furnished in coils.

The hot-rolled strip is suitable for forming into angles for punching into washers or for re-rolling.

COLD-ROLLED STRIP

Cold-rolled strip in monel metal and pure nickel is produced by the manufacturer in any thickness from 0.015 to 0.250 in. Thinner strip is limited to narrow widths.

From thicknesses of 0.015 in. maximum width is 12 in., from 0.018 to 0.034 in. maximum widths are 12 to 16 in. On thickness 0.037 in. and heavier, the maximum width is 18 in. The strip can be supplied in coils approximately 200 ft. long in thickness 0.062 in. and lighter and in 100-ft. coils from 0.070 to 0.125 in. Straight flat lengths are supplied from 0.125 up to 0.250 in. thick. Straight lengths can also be had in gages lighter than 0.125 in. if desired.

The cold-rolled strip can be rolled very close to gage, and in all except annealed tempers has a highly finished surface from the rolls that can be readily polished. Annealed strip has a dull surface but can be polished with reasonable ease. The cold-rolled strip has a very fine grain structure and is particularly well adapted for deep drawing or other cold working.

Cold-rolled strip is supplied in the annealed condition ready for further cold work. It can also be supplied unannealed in a series of tempers up to full hard. The range is well covered by the five tempers designated by the manufacturer as "soft," "skin hard," " $\frac{1}{4}$ hard," " $\frac{1}{2}$ hard" and "full hard."

For all severe drawing-press operations, for spinning, or for the manufacture of intricate moldings of plain metal or metal-covered wood, soft temper, cold-rolled strip should be selected. Harder temper material is for use where stiffness is required and is ordinarily to be used as rolled. The tempers harder than "soft" will not stand much cold work.

SEAMLESS TUBING

Seamless tubing is produced by the manufacturer in pure nickel, but not in monel metal. The pure nickel seamless tubing is made in diameters from $\frac{1}{4}$ to 4 in. and in wall thicknesses from 0.035 up to 0.165 in. The smallest outside diameter in 0.035 in. wall thickness is $\frac{3}{8}$ in. The lightest wall thickness in $\frac{1}{4}$ in. outside diameter is 0.049 in. Similarly, the smaller diameters of tubing are not produced in the thickest wall sizes. The cold-drawn seamless nickel tubing is also produced in iron pipe sizes from $\frac{1}{8}$ to 3 in. One and one-quarter and $1\frac{1}{2}$ in. extra heavy I.P.S. and 2 to $4\frac{1}{2}$ in. standard iron pipe size seamless nickel are also made by the manufacturer in the form of hot-rolled tubing.

All the cold-drawn tubing and cold-drawn pipe sizes are supplied by the manufacturer with a ground finish on the outside, the surface being bright. The hot-rolled pipe carries an oxidized or black surface. Pure nickel seamless tubing and pipe are produced in mill lengths of from 5 to 20 feet.

Nickel seamless tubing can be bent and coiled cold on practically the same limits that apply to other metals. It can be swaged or expanded into headers, and can be welded, brazed, or soldered.

Seamless nickel tubing is finding extensive application in evaporators for alkalies, salts, mild acids and other corrosive products. It is used both to procure durability of equipment and also to insure minimum contamination of products handled. It is widely used in the dairy industry for cooling and warming apparatus.

GAS-WELDED TUBING

Gas-welded tubing is supplied by the manufacturer in monel metal only. This tube is produced by rolling strip into tubular form and welding with automatic gas machines. All the welded tubing is redrawn to shape after welding. This welded seam monel metal tubing is available in sizes from $\frac{1}{4}$ to 4 in. and in wall thicknesses of 0.035, 0.049, 0.065 and 0.083 in. The larger sizes are not produced in the lighter walls, and $\frac{3}{4}$ in. is the smallest diameter in which the 0.083 in. wall is produced. It is supplied in mill lengths of from 5 to 17 ft., and is tested to withstand an air pressure of 250 lb. and to take an expansion of 10 per cent. over a 45° tapered mandrel.

Welded monel metal tubing is unannealed and is made from cold-rolled strip and retains a comparatively bright appearance through the rolling and welding operations. It is also supplied on order with a ground finish on the outside. This type of tubing can also be produced in special shapes, square, rectangular, open-seam, etc.

Welded tubing is used where corrosive conditions require monel metal rather than nickel. It is used for mechanical purposes. Open-seam monel metal tubing has been used for trim in architectural work.

FORGINGS

Forgings in monel metal and pure nickel can be procured from a large number of forging firms throughout the United States and Canada who are familiar with the handling of these metals. The primary manufacturer of the metals will also undertake to supply rough forgings, or rough turned forgings, of large size or unusual difficulty in cases where the outside forging companies are unable to supply the requirements. Monel metal and nickel bolts, nuts and washers are manufactured by a number of firms and the primary manufacturer of the metal is also equipped to supply these items in standard sizes and a limited variety of bolt heads.

Monel metal and pure nickel forgings have the full physical properties of the hot-rolled metal and are utilized to take advantage of the high tensile strength combined with corrosion resistance. Extensive use is made of monel metal bolts and special forgings for acid resistance in pickling plants of the steel industry. Bolts are also finding wide application for outdoor electrical transmission apparatus. In this use high resistance to fatigue and shock, freedom from corrosion-fatigue failures, in conjunction with high mechanical strength and corrosion resistance, make monel metal bolts particularly reliable.

CASTINGS

Monel metal and pure nickel castings are made by the manufacturer to any desired pattern. The castings are ordinarily sand castings; centrifugal cast tubes or rings are also supplied.

Patterns must ordinarily be prepared for monel metal and pure nickel to take care of the necessary shrinkage, which is $\frac{1}{4}$ in. to the foot. On patterns already made for steel, iron or bronze these can be handled in the foundry if a blue print of the finished product is supplied. The foundry will ordinarily lag such patterns to adapt them to monel metal without permanently changing the pattern in any way.

Monel metal castings are also made by a number of jobbing foundries throughout the country. Some precautions and experience are necessary in handling the monel metal or nickel which are both of high melting point. Large sink-heads are necessary as well as care and experience in molding, furnace practice and pouring practice, so that it is ordinarily best to procure monel metal and nickel castings from the primary manufacturer rather than to attempt to produce them locally.

ELECTROLYTIC NICKEL

Nickel of highest purity is supplied in the form of electrolytic cathodes which may be sheared to a desired size. The electrolytic nickel is widely used for the manufacture of alloys such as nickel-silver or white gold where nickel of high purity is required.

ANODES

Nickel anodes are supplied through the platers' supply houses for all sorts of plating and electrodeposition. The nickel anodes are made both cast and rolled.

SHOT AND BLOCK FOR MELTING

Both monel metal and nickel are supplied in the form of shot and cast blocks for remelting. Nickel is supplied in 5, 25 and 50-lb. pigs., and monel metal in 25 and 50 lb. pigs. Monel metal block and shot are chiefly used for monel metal castings. Nickel block and shot are used for melting into various white metal alloy castings; for alloying with brass or bronze, and for alloying with aluminum. The most extensive use of large nickel pigs is for the manufacture of alloy steel and nickel-bearing cast iron.

Wrought Zinc

C. S. TREWIN,* NEW YORK, N. Y.

(Detroit Meeting, September, 1927)

ZINC, in its wrought form, is produced commercially in rolled strip, sheet, wire, rod and tubing. Wire has been made periodically, but due to the fact that slight drafts are necessary, the cost of production is greater than for the more common non-ferrous metals which are made into wire. Notwithstanding the cost, zinc wire has certain special uses for which it is particularly adaptable. Rod has been made both by rolling and extrusion; the product, however, has not indicated great commercial value.

Tubing has been made from strip from time to time by forming a strip around a mandrel and either electrically or gas-welding a longitudinal joint. Recently a tube manufacturer has succeeded in making a fair quantity of this material. Its commercial adaptability is still to be determined but anyone who desires it can obtain quantities of the smaller sizes.

Inasmuch as strip and sheet are commercially the most important, this paper will be devoted to these products.

In the broader sense, zinc is not alloyed. That is, there are no combinations comparable to the various copper, aluminum and nickel alloys. It has been recognized for some time that the lead and cadmium occurring with commercial zinc have some effect on its properties and such alloys as may be said to exist are those made from zines containing varying amounts of lead and cadmium with a relatively low iron content. The foreign rolled zinc will analyze higher in lead than the domestic grades. A representative foreign analysis will run 1.1 per cent. lead, 0.07 per cent. cadmium and 0.02 per cent. iron. The American grades vary from zinc approximating high grade and analyzing 0.08 per cent. lead, 0.002 per cent. cadmium and 0.015 per cent. iron, to the lower grades in which the lead will vary from 0.3 to 1.0 per cent., cadmium from 0.10 to 0.5 per cent. and the iron in the neighborhood of 0.02 per cent.

ROLLED ZINC

Rolled zinc is produced in both the strip (or ribbon) form in which the product is rolled from a single bar in one continuous direction, or sheet in

* Technical department, The New Jersey Zinc Co.

which the product is rolled by the pack method. For strip thicknesses may be obtained from 0.006 to 1.00 in. in coils or flat lengths. Depending on the gage, the maximum width varies from 12 to 20 in., and widths narrower than 12 in. may be obtained in any gage. The length of coils may vary from 100 to 250 ft. in the heavy and medium gages and up to 500 ft. in the lightest gage. In sheet, thicknesses vary from 0.006 to 0.1 in., widths from 18 to 60 in. and lengths from 72 to 144 inches.

TESTS

Because of zinc's extreme sensitiveness to rate of loading, tests must be performed at rates of loading or deformation comparable to those occurring in service. Thus the standard Erickson or Olsen cupping test in which the rate of deformation is 0.3 in. per min. is not applicable because of the low speed and the dynamic ductility test was developed in which the cupping is performed in a commercial press operating at commercial speeds.¹

On the other hand, the tensile test carried out with a pulling speed of 0.25 in. per min. is too rapid to indicate the permissible continuous load for zinc. When this is of importance as in the case of corrugated roofing sheets, static tensile or loading tests must be made. The static tensile tests are performed by applying a series of static loads to tensile specimens under carefully controlled temperature conditions, and for considerable periods of time (days or weeks) observing the elongation by an optical extensometer. The loading tests are conducted with commercial size corrugated specimens upon which predetermined loads are applied over various spans and the deflection at the center of the span measured under selected temperature conditions.

From these tests the following table was determined for safe roof loads per square foot on various purlin spacings for Nos. 13, 14 and 15 gage $\frac{7}{8}$ in. deep corrugation with end lap.

Safe Roof Loads

Loads, Lb./Sq. Ft.	Purlin Spacing—Inches		
	No. 13 (0.032 In.)	No. 14 (0.036 In.)	No. 15 (0.040 In.)
30	39½	41	42
40	36½	37½	39
50	33½	35½	36½

For single span sheets or sheets without end lap reduce purlin spacings given by 20 per cent.

Corrugated zinc sheets lighter than 13 gage are not recommended for use over purlins.

¹ C. H. Mathewson, C. S. Trewin and W. H. Finkeldey: Some Properties and Applications of Rolled Zinc Strip and Drawn Zinc Rod. *Trans.* (1920) **64**, 305.

Temper (stiffness) is determined by a special machine which wraps a flat specimen around a mandrel and then allows one end of the specimen to spring from the mandrel. The angular deflection of the end of the specimen is measured to indicate the temper.

The ability of zinc to withstand cold bends is also of importance. We have in the course of development a machine to evaluate this property. Inasmuch as it has yet to be given a thorough try-out it has not been described.

It is important to note that in these testing methods, wherever rate of loading is a factor, the human element has been eliminated by the use of motor-driven units.

The physical properties for commercial rolled zinc tested for dynamic ductility and temper, the method of determining the end point of the tests and the commercial variations in thicknesses and widths may be found in the recently adopted A. S. T. M. Tentative Specifications for Rolled Zinc.

RANGE OF PHYSICAL PROPERTIES

On account of the limited range of useful alloys, the physical properties do not vary to as great an extent as will be found in other non-ferrous metals and their alloys. There are, however, important variations in properties possible within certain limits; for instance, temper may be increased in a limited range without great sacrifice of ductility and cold bends. If, however, relatively great stiffness is required, high ductility is sacrificed and vice versa. For specific application it has therefore been necessary to study carefully the conditions of service and recommend to the consumer a product which will meet his demands.

The surface of the strip metal as it comes from the rolls may have as a result of hot rolling a bright smooth finish. Cold rolling results in a duller surface. Roll marks are of course present on all strip. In the case of sheet the finish is a dull planish which gives a very smooth and satisfactory surface for many uses or a higher finish, bright and particularly smooth, which is well adapted to subsequent nickel plating and is of considerable value in such applications as lithographers' plate and photo-engravers' stock.

STRIP ZINC

Strip zinc, due to its longer length, is generally preferred for automatic forming operations. For deep drawing operations a soft rolled strip of high-grade zinc, having a high dynamic ductility value and low temper, is used in nearly all cases. For certain applications such as running board molding and weather strip, a stiffer temper, combined with high cold bend is more desirable. The product, which is most adaptable for drawing operations, has a limited application in certain fields due to its lack

of stiffness. Certain developments indicate the possibility of the stiffening of this product with the retention of its excellent ductility.

Due to the low annealing temperature of high-grade zinc, which makes it practically self-annealing at room temperature, it is unnecessary to anneal products drawn from this grade of strip between successive drawing operations. It has been found desirable to maintain the stock and dies for these operations at a fairly warm room temperature, 80° to 85° F. A serious drop in ductility may be encountered if the metal is drawn or formed at temperatures below 60° F. Actual annealing of the stiffer cold-worked grades of rolled zinc occurs at temperatures in the neighborhood of 212° F. and usually results in a grain coarsening with corresponding detrimental changes in important physical properties.

DETERMINATION OF DESIGN FOR SUCCESSIVE OPERATIONS

In the deep drawing of zinc the metal is formed during the successive steps into the desired shape without a reduction in the thickness of the stock at any time. The following directions have been found useful in determining the design of successive drawing operations:

1. Compute the total area of the finished cup and add to this sufficient area to allow a trim of $\frac{1}{4}$ in. on the finished cup.
2. Calculate the diameter of the circle of a blank having the above area.
3. The reduction in diameter² from the blank to the first cup should not exceed 40 per cent. of the diameter of the blank.
4. The reduction in diameter² of succeeding cups should not exceed 20 per cent. of the preceding cup.
5. Die clearances should be twice the thickness of the stock plus 0.001 or 0.0015 in. Filets should be generous.
6. Soapy water is a very satisfactory lubricant.

When machining is necessary particularly with the purer grades of zinc an excessively long chip is encountered. This has been successfully overcome by the use of tools with a greater rake than is normally used.

² A flange must be included in the diameter.

Commercial Forms and Applications of Aluminum and Aluminum Alloys

By P. V. FARAGHER,* NEW KENSINGTON, PA

(Detroit Meeting, September, 1927)

A METAL or alloy finds its place in commerce in proportion to its ability to serve certain purposes better and more economically than other materials. While there is some overlapping of the fields of application of the various metals under discussion in this symposium, each one has its uses for which it is especially adapted. While aluminum is the most recent of the metals to enter the field, the development of the industry has been based on its peculiar properties, by virtue of which new uses for non-ferrous metals have been created. There has been substitution of this new metal for other members of the group but there has been a far greater development in entirely new fields.

In common with the other non-ferrous metals, aluminum is resistant to atmospheric corrosion. It also withstands the action of many of the common chemical reagents, strongly alkaline substances being the notable exceptions. The outstanding properties on which the application of aluminum is based are its low specific gravity and its ease of fabrication into the forms in which it is used.

It is noteworthy that this property of specific lightness is retained in all the commercial aluminum-base alloys. This statement does not apply to aluminum bronze; this is more properly a copper-base alloy, since aluminum enters into its composition to the extent of only about 10 per cent. None of the commercial casting alloys of aluminum has a density exceeding that of the parent metal by more than about 10 per cent., and some are actually lighter. In the so-called "strong alloys" of aluminum in which strengths comparable to that of mild steel are developed by heat treatment, the greatest increase in density is only slightly more than 3 per cent., and one of these, also, is lighter than aluminum.

This property of lightness combined with the desirable mechanical properties of the alloys, makes aluminum especially suited for parts of moving assemblies where saving in power, as well as a decrease in stresses resulting from inertia and vibration, are of importance.

* Technical Direction Bureau, Aluminum Co. of America.

THE ECONOMY OF ALUMINUM

Even where the property of lightness is not essential to the service which the part is to perform, the low specific gravity enters into the cost considerations; because of its lightness, the metal cost may be lower than would result from the use of a metal whose price per pound was very much less. In some applications, the greater ease of machining or of finishing must also be taken into consideration in order that aluminum shall be considered from the standpoint of economy. These points will be taken up again in connection with certain specific cases.

Other properties which contribute to the demand for aluminum are its high conductivity for heat and electricity, and the fact that its compounds are colorless and are not harmful to the human organism, at least in amounts considerably greater than those which may be present from the use of aluminum in the preparation or packing of foods or beverages. The ease with which the metal can be polished to produce a pleasing and enduring finish is also of interest for some purposes.

The term "aluminum" is commonly used rather loosely to designate the alloys as well as the metal of commercial purity, for example, "aluminum pistons" or "aluminum castings." Similarly, the commercially pure metal containing from 99.0 to 99.3 or 99.4 per cent. aluminum, the remainder consisting largely of iron, silicon and copper introduced in the process of electrolytic reduction, is called "pure aluminum" when it is desired to distinguish it from its alloys.

EFFECT OF IMPURITIES IN ALUMINUM OF HIGH PURITY

A study of the properties of aluminum of very high purity (99.983 per cent. aluminum) has shown that the few tenths of a per cent. of accidental impurities which are present in the commercial grade exercise a marked influence on its properties. The tensile strength of commercially pure aluminum is approximately 50 per cent. greater than that of the high purity metal, and the behavior toward certain reagents is materially altered.¹ Similar differences have been reported for some of the other non-ferrous metals.

In one sense of the word, commercially pure aluminum is to be considered as a very dilute natural alloy. This metal shows a considerable improvement in tensile strength, yield point and hardness, together with some loss in ductility and in chemical resistance. The mechanical properties of this metal which is commonly, if not most accurately, designated as "pure aluminum" are substantially as shown below:

¹J. D. Edwards: Properties of Pure Aluminum. *Trans. Am. Electrochem. Soc.* (1925) 47, 287.

Tensile Strength.....	12,000 to 16,000 lb. per sq. in.
Yield Point.....	4,000 to 7,000 lb. per sq. in.
Elongation.....	30 to 45* per cent. in a gage length equal to four times the diameter of the test speci- men.
Brinell Hardness.....	10 mm. ball, 500 kg., load 22 to 27.

* Because of the influence of the cross-sectional area of the test specimen on the measurement of elongation when a fixed gage length is used, elongation values will be given for a gage length proportional to the diameter of the specimen or the approximate dimensions to which the values apply will be indicated. For thin aluminum sheet or small wire, the elongation, as commonly measured, in a 2-in. gage length may be as low as 15 per cent.

The rather wide range of values for the various properties is occasioned by the relatively wide limits on "commercial purity" and by the effect of variations in metal structure brought about by the rate of chilling in the case of castings or by the nature of the working and subsequent annealing operations to which the metal may have been submitted.

COMMERCIALLY PURE ALUMINUM

Commercially pure aluminum is practically never used without the addition of an alloying element in the manufacture of commercial castings, because of its relatively low strength and because of its difficult foundry characteristics. The exceptions which make necessary the reservation in this statement are those few cases in which the electrical or chemical properties of the relatively pure metal require its use. This metal, called 2S in accordance with the principal domestic manufacturer's nomenclature, is, however, fabricated into all the forms in which metals are commonly supplied; to enumerate: sheet both flat and strip, plate, foil, bar, rod, wire, seamless tubing and pipe, molding and shapes both extruded and rolled, rivets, stampings, ingots of various forms and special apparatus.

Most of these products are supplied in various tempers, the increase in hardness being accomplished by strain-hardening the metal by cold work. Some few of these products from the nature of the fabricating process are not produced in all tempers, or at least not in all sizes. Extruded material will naturally be in substantially the soft temper since the temperature of extrusion is in excess of the instantaneous annealing temperature of the metal. Bar and rod are not regularly produced in the full hard temper in sizes larger than $\frac{3}{4}$ in., in the half hard temper the maximum size is $2\frac{1}{2}$ in. Larger sizes could be produced in these tempers if there were a demand for them, but where higher mechanical properties are desired, alloy rod is usually supplied.

The standard tempers for aluminum with the approximate mechanical property ranges are shown in Table 1. These tempers are produced by

reducing the cross-sectional area of the metal by appropriate amounts of cold work subsequent to the final annealing operation.

TABLE 1.—*Standard Tempers and Approximate Property Ranges of Aluminum*

Temper	Tensile Strength, Lb. per Sq. In.	Elongation,* Percentage in 2 In.
Soft	12,000 to 16,000	30 to 45
$\frac{1}{4}$ Hard	14,000 to 18,000	5 to 10
$\frac{1}{2}$ Hard	16,000 to 20,000	3 to 7
$\frac{3}{4}$ Hard	19,000 to 23,000	1 to 4
Hard	22,000 (minimum)	1 to 4

* Elongations obtained on sheet in Brown and Sharpe gages 10 to 28 using the test specimen recently adopted by the American Society for Testing Materials, in the intermediate tempers, the specimen is taken parallel to the direction of rolling. Using standard $\frac{1}{2}$ -in. test specimens, these elongation values would be very substantially increased.

In producing sheet in these various tempers, the amount of cold work is determined by the change in thickness; since there is very little widening of the sheet in the rolls, the change in cross-sectional area is proportional to the change in gage. In the case of flat sheet, the number of gage numbers reduction subsequent to the final annealing operation is as follows: 2 gage numbers for $\frac{1}{4}$ hard, 4 gage numbers for half hard, 8 gage numbers for $\frac{3}{4}$ hard and a minimum of 12 gage numbers for full hard. In the case of strip rolling, it has been found that there is a slight difference in the reduction required to produce the same tensile strength. This difference is probably due to the difference in the rate at which the thickness is reduced in the two processes. For bar and tubing, it is necessary to calculate the areas at annealing gage which will give corresponding percentages of reduction in the finished product.

There is some overlapping of the mechanical property limits for the various tempers. The explanation for this is similar to that given previously when discussing the properties of the annealed or cast metal: variations in chemical composition and in the annealing operation, and in addition, the variations from the desired thickness at either the annealing gage or the final gage, which are inevitable in commercial rolling practice.

Sheets in either the $\frac{1}{2}$ hard, $\frac{1}{4}$ hard or soft tempers can be bent flat on themselves in any direction without cracking. This fact is mentioned since it is a more accurate indication of the ductility or "workability" of the metal than is the elongation. This latter property is very appreciably lower in the intermediate tempers when the test specimen is taken perpendicular to the direction of rolling, so much so that it fails to serve adequately to distinguish between the tempers.

The effect of strain-hardening the metal is shown quite clearly in Table 1. The increase in tensile strength through the range of reductions shown is very closely proportional to the reduction in cross-sectional area; for higher reductions, the rate of increase becomes progressively greater than would be expected from this proportional relationship. This connection between rate of reduction by cold work and increase in tensile strength has been studied by R. L. Templin, Chief Engineer of Tests of the Aluminum Co. of America, who has derived an empirical formula which is in very close agreement with the data. The tensile strengths for the different tempers are so chosen as to be stronger than the annealed metal by the appropriate fraction ($\frac{1}{4}$ for $\frac{1}{4}$ hard, etc.) of the range in strength between full hard and soft metal.

3S ALLOY

Except the so-called "strong alloys" in which the mechanical properties are susceptible of improvement by heat-treatment processes, there is only one alloy which is produced in this country in a wide variety of wrought forms. This alloy, called 3S by the principal producer, contains approximately $1\frac{1}{4}$ per cent. manganese in addition to the usual impurities of commercial aluminum. It is obtainable in practically all of the forms enumerated for the commercially pure metal. Alloys containing small amounts of copper, or copper together with manganese or zinc and occasionally an alloy of nickel with aluminum may be rolled into sheets or rods but the tonnage is small.

The addition of manganese to commercial aluminum to form 3S alloy is practically without effect on the corrosion resistance; in some cases this alloy appears to give even somewhat better results than 2S. This is noteworthy, since, in general, the gain in mechanical properties resulting from the alloying operation is attended with some loss in the ability to withstand severe corrosive conditions.

TABLE 2.—*Mechanical Properties of Aluminum-manganese (1.25 Per Cent.) Alloy (3S)*

Temper	Tensile Strength, Lb. per Sq. In.	Elongation,* Percentage in 2 In.
Soft	15,000 to 18,000	15 to 30
$\frac{1}{4}$ Hard	18,000 to 22,000	5 to 8
$\frac{1}{2}$ Hard	20,000 to 24,000	2 to 6
$\frac{3}{4}$ Hard	24,000 to 29,000	1 to 4
Hard	27,000 (minimum)	1 to 4

* Minimum values obtained with sheet in gages 10 to 28; sheet in intermediate tempers tested parallel to the grain. Standard $\frac{1}{2}$ -in. round specimens show distinctly higher values.

In this alloy as in commercially pure aluminum, the various tempers are produced by cold-working the metal after annealing. The same standard tempers are supplied, the mechanical properties being in accordance with Table 2.

In general, the statements made above concerning commercially pure aluminum apply also to this alloy. It is of interest, however, that in this case there is less difference between the properties produced by a given amount of reduction in the flat-rolling and strip-rolling processes than there is in the case of the 2S metal. This alloy gives appreciably higher properties, particularly in the harder tempers, with only a small decrease in elongation as compared with 2S metal.

USES FOR COMMERCIALLY PURE ALUMINUM

Commercially pure aluminum or 2S, has a great diversity of uses. For drawing, stamping and spinning, for the manufacture of cooking utensils, tanks and containers of various types, this metal in the form of sheet or strip is used most extensively. In fact, the producers supply a large tonnage of sheet ready blanked or sheared in the form of "circles" ready for use on draw presses or spinning machines. In order that the finished part shall be as stiff as possible, the hardest temper which will withstand the fabricating operation without excessive loss due to cracking or tearing, is chosen. The greatest production for these purposes is in the soft and in the half hard tempers.

"Flat sheet" has a bright planished surface while the strip sheet is slightly gray in appearance and shows superficial surface striations or "grain" in the direction of rolling. Strip sheet is readily polished, however, to produce the bright finish which is seen on high grade aluminum ware.

For automobile body work, flat sheet in a temper intermediate between the standard half hard and three-quarter hard is used. For the gages which are most commonly used, the manufacture is somewhat simpler than for the half hard temper and the added strength and hardness are desirable. The material retains sufficient ductility or "workability" to permit the necessary forming operations.

The manganese alloy "3S" is used much the same as "2S," where somewhat greater strength or stiffness is desired and the forming operation is not too severe for the metal to withstand without failure. In the hard temper, the properties of this alloy are adequate for a considerable range of uses. The yield point is about two-thirds that of the strong alloys, hence, where little forming is to be done and the highest properties are not essential, this alloy is extensively used.

Both "2S" and "3S" can be welded, using the oxy-hydrogen flame and a suitable flux, although somewhat more skill is required in handling

3S. Special apparatus for use in the chemical or food industries is made up from sheet or plate, tubing, etc., formed into the desired shape and assembled by welding, or by a combination of welding and riveting where higher pressures may be encountered.

COMMERCIAL SIZE LIMITS OF ALUMINUM PRODUCTS

The listing of commercial size limits on various products presents some difficulties, and before attempting such a list, some word of explanation must be given. The commercial size ranges do not, in most cases,

TABLE 3.—*Foil*,
[Special Aluminum]

Thickness (In.) (Calculated from Covering Area)	Covering Area, Sq. In. per Lb.	Widths (In.)	Remarks
0.00035 to 0.005 (Tolerance ± 10%)	29,200 to 2,050 (Tolerance ± 10%)	$\frac{7}{8}$ to 15 (Tolerance ± $\frac{1}{32}$ in.)	Furnished in coils wound on mandrels of aluminum tubing $1\frac{5}{8}$ in. I. D. or cut in rectangles having a maximum length of 40 in.; plain, paper interleaved or wax paper backed; also embossed, printed or lacquered in standard colors.

TABLE 4.—*Flat Sheet**

[Commercially Pure Aluminum (2S) and Aluminum Manganese Alloy (3S)]

Thickness		Thickness Tolerance Plus or Minus				
In.	B. & S. Gage (Approximate)	Widths			Widths,† In.	Lengths, In.
		20 In. and Less	Over 20 to 36 In.	Over 36 to 60 In.		
0.005 to 0.013	36 to 28	0.0015	0.0015		$\frac{1}{4}$ to 36	up to 180
0.014 to 0.018	27 to 25	0.002	0.002	0.002	$\frac{1}{4}$ to 40	up to 180
0.019 to 0.029	24 to 22	0.002	0.002	0.003	$\frac{1}{4}$ to 48	up to 180
0.030 to 0.072	21 to 14	0.0025	0.0025	0.003	$\frac{1}{4}$ to 60	up to 180
0.073 to 0.144	13 to 10	0.003	0.0035	0.004	$\frac{1}{4}$ to 60	up to 180
0.115 to 0.219	9 to 4	0.005	0.006	0.007	$\frac{1}{4}$ to 60	up to 180
0.220 to 0.250	3 to 2	0.007	0.008	0.009	$\frac{1}{4}$ to 60	up to 180

* Special rolling practice is required to produce: $\frac{3}{4}$ hard sheet thicker than 0.162 in. (6 ga.); hard sheet thicker than 0.102 in. (10 ga.).

† Widths up to 105 in. and lengths up to 25 ft. can be supplied in thicknesses over 0.102 in. except that the maximum weight of the sheet shall not exceed 400 lb. These limits, exceeding the ordinary commercial limits, may be commercial in suitable quantities.

TABLE 5.—*Strip Sheet*

[Commercially Pure Aluminum (2S) and Aluminum Manganese Alloy (3S)]

Thickness		Thickness Tolerance Plus or Minus			
In.	B. & S. Gage (Approximate)	Widths		Widths, In.	Lengths
		$\frac{1}{4}$ to 12 In.	Over 12 to 27 In.		
0.005 to 0.010	36 to 30	0.001		$\frac{1}{4}$ to 14	Supplied in coils or flattened. Continuous strips or cut to length.
0.011 to 0.016	29 to 26	0.0015		$\frac{1}{4}$ to 16	
0.017 to 0.040	25 to 19	0.002	0.0025	$\frac{1}{4}$ to 18	
0.041 to 0.102	18 to 10	0.003	0.003	$\frac{1}{4}$ to 35	

TABLE 6.—*Plate*

[Commercially Pure Aluminum (2S), and Aluminum Manganese Alloy (3S)]

Thickness, In.	Widths	Lengths	Remarks
(Tolerance ± 4 per cent. of nominal) 1.0 to 0.26	*	*	Maximum weight of single plate 400 lb. Maximum commercial thickness for tempers other than soft: $\frac{1}{4}$ Hard not over $1\frac{3}{16}$ in. $\frac{1}{2}$ Hard not over $\frac{5}{8}$ in. $\frac{3}{4}$ Hard not over $1\frac{3}{32}$ in. Hard not over $\frac{1}{4}$ in.

* Dimensions are largely governed by the weight and dimensions of the largest commercial rolling ingot. Maximum length = $\frac{7}{\text{Thickness}} \times 20$ in. up to a maximum of 300 in. (25 ft.). Maximum width will vary with the thickness and length of the plate, from 105 in. downward. Slabs thicker than 1 in. can be produced although metallurgical characteristics will depend upon the amount of rolling done on the ingot.

TABLE 7.—*Rolled Rod and Bar*

[Commercially Pure Aluminum (2S), and Aluminum Manganese Alloy (3S)]

Shape	Maximum Dia. or Distance across Flats (In.)		
	Temper		
	Soft	Half Hard	Hard
Round.....	$3\frac{1}{4}$	$2\frac{3}{4}$	$\frac{3}{8}$
Square.....	$1\frac{1}{2}$	$1\frac{1}{2}$	$\frac{3}{8}$
Hexagon.....	$1\frac{1}{2}$	$1\frac{1}{2}$	$\frac{3}{8}$
Rectangles*.....	$1\frac{1}{2}$ by 2	$1\frac{1}{2}$ by 2.	$\frac{3}{8}$

* Larger sizes may be manufactured by sawing plate to desired width, in tempers as noted in Table 4.

represent the maximum possibilities but rather the limits which are readily obtained in normal routine operation. By a modification of this practice, which may be warranted if a sufficient poundage is involved, the commercial limits may be extended. Moreover, advances in the fabricating practice are continually being made, and any statement as to limiting sizes may be obsolete almost before it is published. With this preliminary note, the tables indicating size ranges are presented.

While the practice in the sheet steel industry of manufacturing sheets only in definite gages and in standard sizes is desirable from the standpoint of operating economy, this practice has not as yet been possible in the aluminum industry because of the varied demands which arise in developing new uses and applications for a metal. Consequently, it may be stated that aluminum sheet and plate are rolled in any thickness and sheared to any size which is within the limiting ranges. Naturally, only certain standard sizes and gages are carried in warehouse stocks.

EXTRUDED SHAPES, MOLDING, RODS AND BARS

Limiting dimensions vary with the shape; heavy sections can be extruded in sizes up to 5 in.; in certain lighter sections the greatest dimension may be as much as 6 in. Minimum thickness of sections is usually not less than 0.125 in. (Except when stock dies are available, commercial production of shapes is limited to quantities sufficient to warrant manufacture of extrusion die.)

TABLE 8.—*Dimension Tolerances of Rod, Bar and Shapes*
[Commercially Pure Aluminum (2S) or Aluminum Manganese Alloy (3S)]

Nominal Dimension, In.	Rolled or Drawn Tolerance Plus or Minus, In.	Extruded* Tolerance Plus or Minus, In.
Up to 0.125	0.002	0.007
0.126 to 0.500	0.002	0.010
0.501 to 1.000	0.003	0.015
1.001 to 1.500	0.005	0.020
1.501 to 2.000	0.008	0.020
2.001 to 3.25	0.008	0.025
3.25 to 6.00		0.025

* Closer tolerances can be met by following the extrusion operation with a sizing draw.

Extruded material will be substantially in the soft temper.

TUBING

Seamless tubing is regularly made in sizes $\frac{1}{4}$ to $6\frac{7}{8}$ in. and in wall thicknesses from 0.022 to 0.300 in. (Stubbs gages 1 to 24), the wall thickness range for a given diameter varying with the diameter. The maxi-

alum length is 45 ft. with the limitation that the maximum weight of the tube shall not exceed 55 lb. In the annealed temper the length is further limited by available furnace equipment, to 30 ft. Similarly, the harder tempers cannot be produced in the largest size tubes nor in tubes in which the ratio of diameter to wall thickness is too great.

STRONG ALLOYS

Reference has been made in the preceding pages to the strong alloys, of which there are several in commercial production. This term is usually used to designate the wrought alloys because of the fact that the heat treatment process, to which these alloys owe their exceptional properties, is most effective in material in which the cast structure has been destroyed by working. Some very striking results are obtained with certain casting alloys, however, and these will be discussed under that heading.

These strong alloys were developed as a result of the efforts to obtain materials having tensile properties comparable with those of steel and at the same time, having the lightness and other valuable properties of aluminum. The measure of success which has been attained will be seen by reference to Table 9. This table does not purport to list all of the alloys in this class but includes only those for which mechanical data are available from actual commercial production and which can be had readily in this country. The nominal compositions are shown in Table 10.

The various tempers in these alloys are obtained by variations in the heat treatment to which they are subjected, and not as in the case of 2S and 3S by strain hardening. For a proper understanding of the table, a brief explanation of the symbols and the corresponding heat treatment is desirable.

These materials, like most other metals, strain harden when they are cold-worked, consequently, after a certain amount of reduction by cold work, they must be annealed before they can be worked further. This annealing is accomplished by heating to a suitable temperature and allowing the metal to cool. The metal is then in its softest state, and in the case of the alloys of the Aluminum Co. of America, this condition is indicated by the symbol 0.

HEAT TREATMENT

In order to develop the maximum properties of the alloy, it is heated to the proper temperature, quenched and then aged. This heat-treating temperature is considerably higher than the annealing temperature referred to above. The heating and quenching develop tensile properties very considerably higher than those for the alloy in the annealed state.

The aging process is necessary, however, to produce the high strength, yield point and hardness which are desired for most uses. Some of these alloys age spontaneously at ordinary temperatures, the process being practically complete in a few days, the others must be subjected to a second heating operation or artificial aging to accomplish the maximum results, although with one exception (25S) all experience some improvement at ordinary temperatures. The alloy which has been treated to produce its maximum properties is designated by the symbol "T." In case the alloy has not been given its characteristic aging, the temper is called "as quenched," designated as "W." This symbol is used with 51S and Special 17S which have been heated and quenched and then kept at ordinary temperatures even though some hardening does occur, since they are still capable of considerable improvement by their characteristic aging processes.

TABLE 9.—*Mechanical Properties of Strong Aluminum Alloys*

Alloy	Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elonga- tion, Per- centage in 2 In.	Brinell Hardness 500 Kg. Load—10 Mm. Ball	Order in Relation to Increasing Radius for Cold Bends
51SO.....	14,000 to 19,000	4,000 to 6,000	15 to 30	25 to 32	1
51SW.....	30,000 to 40,000	15,000 to 20,000	20 to 30	55 to 70	6
51ST.....	45,000 to 50,000	30,000 to 40,000	10 to 18	90 to 100	12
25SO.....	23,000 to 35,000	7,000 to 12,000	12 to 20	45 to 55	5
25SW.....	45,000 to 53,000	15,000 to 30,000	15 to 22	68 to 85	9
25ST.....	55,000 to 63,000	30,000 to 40,000	16 to 25	90 to 105	11
17SO and an- nealed duralu- min.....	25,000 to 35,000	7,000 to 10,000	14 to 22	45 to 55	4
17ST and duralu- min.....	55,000 to 63,000	30,000 to 40,000	18 to 25	90 to 105	10
B17SO.....	20,000 to 25,000		20 to 28	30 to 40	3
B17ST.....	42,000 to 50,000	20,000 to 25,000	20 to 28	65 to 85	8
A17SO.....	20,000 to 25,000		20 to 28	30 to 40	2
A17ST.....	35,000 to 45,000	15,000 to 20,000	20 to 28	55 to 75	7
Special 17SO.....	25,000 to 35,000	7,000 to 10,000	12 to 20	42 to 55	4
Special 17ST.....	63,000 to 70,000	50,000 to 55,000	8 to 14	95 to 125	13

Note.—Certain modified grades of duralumin are also manufactured. Alloys 51S and 25S are covered by patents owned by Aluminum Co. of America.

As was stated previously, the maximum benefit of heat treatment depends upon a thorough working of the alloy prior to the heating and quenching. In the case of certain larger sizes of products, it is not feasible to introduce this optimum amount of work in present commercial production. With a sufficient demand for such materials to warrant the

installation of more suitable equipment and operating methods for their production, further improvement can doubtless be produced.

TABLE 10.—*Nominal Compositions of Strong Alloys*

Alloy	Copper, Per Cent.	Manganese, Per Cent.	Magnesium, Per Cent.	Silicon, Per Cent.
17S and duralumin.....	4.0	0.5	0.5	
25S.....	4.5	0.8	0.0	0.8
51S.....			0.6	1.0
A17S.....	2.5		0.3	
B17S.....	3.5		0.3	
Special 17S.....	4.0	0.6	0.5	1.25

Note.—Composition specifications include a minimum aluminum content so chosen as to permit the normal impurities, and in some cases, small additions of other elements for specific purposes. Where not otherwise indicated, iron and silicon are present in amounts usually found in commercial aluminum.

The mechanical property data as given in Table 9 are, therefore, to be considered as applying to products in the intermediate sizes or thicknesses. Heavier or thicker material may show tensile strengths lower than the minimum listed, by some few thousand pounds per square inch, and elongations lower by a few per cent. One factor which contributes to the lower elongation of heavier bar or sheet is the fact that the straightening or flattening operation after the quench introduces relatively more strain hardening with its very pronounced effect on the elongation, than is experienced with thinner stock. A similar effect though not so great is observed with wide sheets, even in thinner gages. Also, very thin sections will show lower elongations due to the effect of the cross-sectional area of the test specimen on this property. To be specific, sheets in thicknesses 0.021 to 0.128 in., that is in Brown and Sharpe gages heavier than 24 to 8 inclusive, and rolled bar up to 1 in. may be expected to have the properties indicated; in extruded sections even larger sizes fall in this range.

Range of Strengths

These alloys, while of relatively recent development, have already found very extensive application as materials of construction, possessing as they do a very high ratio of strength to weight. The most generally used are 17S and duralumin, 25S and 51S. As will be seen by reference to Table 9, these alloys in their various tempers cover quite completely the entire range of strengths from a value only slightly greater than that of commercially pure aluminum up to 70,000 lb. per sq. in., the yield points varying correspondingly. The elongation and the ability to withstand various forming operations are dependent both on the alloy and on the temper.

Only a few of the outstanding characteristics of the various members of the group can be enumerated. From the standpoint of corrosion resistance, none of these alloys is the equal of commercial aluminum, the gain in mechanical strength has been attended in every case with some loss in this property. The temper of the metal has a very great influence on the ability to withstand attack. In every case the best resistance is possessed by the metal which has been heated and quenched without a subsequent heating operation either to artificially age or to anneal the alloy.

Strength, Ductility and Corrosion Resistance of 17S and Duralumin

This means that 17S and duralumin show the highest combination of strength and ductility together with maximum corrosion resistance. Consequently, where even superficial attack would be serious, as in thin highly-stressed sections such as are used in air craft, these alloys are universally employed. In addition, a protective coating is used to further insure their safety.

However, in ordinary applications, all of these materials in all tempers possess adequate corrosion resistance as is evidenced by their satisfactory performance in a wide variety of uses. Some of the other alloys are more easily manufactured and are, consequently, less expensive than duralumin or 17S; it is only natural that they should find a continually increasing use in those applications where their properties are adequate.

The tensile properties of 25S alloy in the fully heat-treated temper (25ST) are nearly the same as those of 17S or duralumin. It is not so easily formed, however, and where a difficult drawing or bending operation must be withstood, it is not quite the equal of those alloys. Where these problems do not enter, it may frequently be substituted because of its lower cost. When properly handled, 25S can be forged readily, probably the greatest production of commercial forgings is from this alloy.

The alloy 51ST does not have as high a strength as 17ST and 25ST by about 10,000 lb. per sq. in., although its yield point is substantially the same. This rather remarkable fact is responsible for the extensive use of this metal. In the fully heat-treated temper, it is not easily worked, but this shortcoming can be overcome by carrying out the fabrication processes in the "as quenched" temper in which condition it is considerably more ductile than 17ST or 25SW. The finished part can then be artificially aged to develop the maximum properties of the alloy.

The modified grades of 17S—A17S and B17S—were developed to supply materials capable of withstanding more severe fabricating operations than are possible with 17S or duralumin. Special 17ST, on the other hand, is used where the maximum possible strength and yield point are desired. Here again, the forming possibilities are limited, but as in

the case of 51S, the metal may be formed in the "as quenched" temper (Special 17SW) and the artificial aging be performed on the finished part.

It is not always possible to state in advance just which of these alloys is best suited for a given case. It is usually necessary to determine by actual trial which can be used most satisfactorily and still give the properties required in service. For automatic screw machine work, 17ST or duralumin rod has been found to give the best results. Forgings are usually made from 25S and 51S although duralumin is also used for this purpose.

STRUCTURAL SHAPES—HOT-PRESSING OF 17S

One of the interesting recent developments is the hot-pressing of 17S to form angles, channels and other structural shapes from heavy plate. Such heavy material cannot be bent cold around a sharp angle, but at higher temperatures, the bend is easily accomplished. The forming

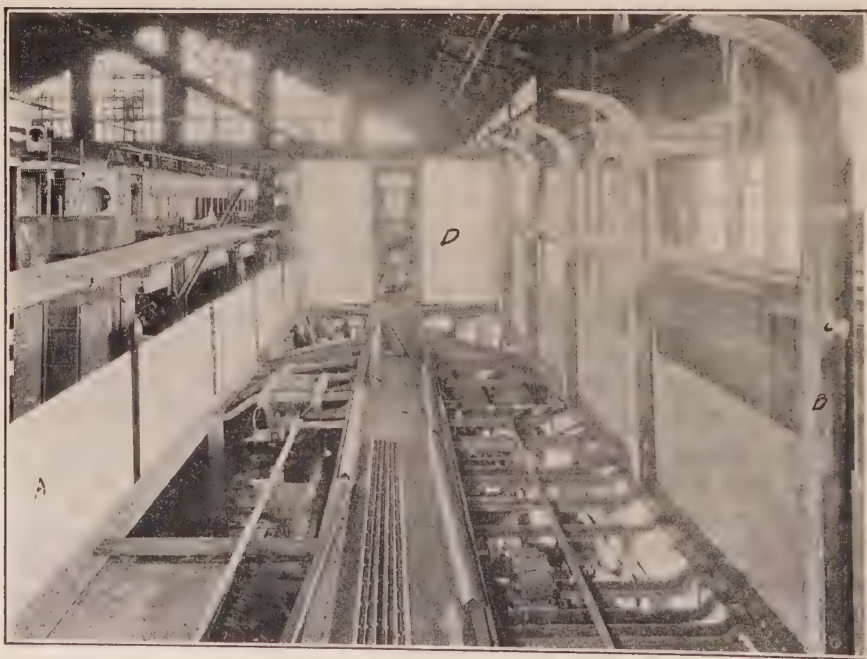


FIG. 1.—RAILWAY PASSENGER CAR IN PROCESS OF CONSTRUCTION BY THE PENNSYLVANIA RAILROAD, SHOWING USE OF ALUMINUM AND ITS ALLOYS: A, 17ST SHEET; B, HOT-FORMED 17ST; C, WINDOW BRACKET OF 195 H-T CASTING; D, ALUMINUM SHEET.

temperature may frequently be in the range of heat-treating temperatures, and the cooling in the forming dies proves to be a very effective quench. The result is that the forming and heat-treating are accomplished in the same operation, and there has been no warping or twisting

of the material as would be experienced in the water quench used in the usual heat treatment operation. Such sections have been used in the construction of railway passenger cars (Fig. 1), street cars, buses and the like, and this application is increasing in amount.

Standard structural shapes are also produced by extrusion in sizes up to about 5 in. The maximum lengths are determined by the weight of the billet which can be extruded—approximately 85 lb. of finished product—or by the available heat-treating equipment; which at present places a limit of about 24 ft. on the length on the alloys which do not require artificial aging. Work is in progress at the present time to increase this length, and it is anticipated that in a short time this limit will be set by the ability to straighten the shapes after heat treatment except as the weight limitation may enter. It is probably only a question of time before this latter restriction will be removed by the development of rolled shapes starting with larger rolling ingots. In 51ST, 25ST and Special 17ST where artificial aging is required, the maximum length is 16 feet.

“Y” ALLOY

The copper, nickel, magnesium alloy with aluminum commonly known as “Y” alloy, while stated to be satisfactory for the manufacture of forgings, is not used in this country except for castings.

COMMERCIAL FORMS OF STRONG ALLOYS

These alloys are manufactured in a wide variety of forms, in fact, the list is nearly identical with that given previously for commercially pure aluminum. The thicknesses for sheet and plate range from about 0.008 to 2.5 in. Even thinner material has been produced but this can hardly be considered commercial at the present time. The widths and lengths which can be produced vary with the gage as may be seen by reference to Tables 11 and 13. Again it should be stated that these tables represent the normal commercial limitations and are not necessarily the maximum sizes that can be produced. The thickness tolerances vary from ± 0.0015 in. for thin sheet to ± 0.004 in. for very wide sheet 0.091 in. thick; in heavier sheet and plate, the tolerance is ± 5 per cent. of the thickness.

Tubing

Tubing is regularly manufactured in diameters from $\frac{1}{4}$ to 4 in., the wall thicknesses varying from 0.028 to 0.165, the more usual alloys being 17S and duralumin, 51S and 25S. Not all wall thicknesses in this range are possible with all diameters of tubing; as the diameter increases, the minimum and maximum wall thicknesses increase correspondingly. In addition to round tubing, other shapes are produced, for example, square, rectangular, oval, “stream line” and other special shapes. Even larger sizes than 4-in. are manufactured in 51S alloy due to its greater ease of

working in the softer tempers, in fact, the size ranges for 2S and 3S apply to this alloy, also. The diameter tolerances vary from ± 0.003 in. for the small sizes to ± 0.010 in. for the largest tubes; the tolerances are applied to the pi-tape reading or to the mean of two readings taken at right angles to each other. Individual readings may deviate from the nominal by an amount double these tolerances. The wall thickness may deviate from the nominal by ± 10 per cent. of the thickness. The maximum lengths are determined by the weight of the bloom, 40 lb., or by the available heat-treating capacity: 24 ft. where aging is not required and 16 ft. for 51ST, 25ST and Special 17ST.

TABLE 11.—*Strong Alloy Plate*

Width, In.	Maximum Length, In.				
	Thickness of Plate				
	2 In.	1.5 In.	1 In.	0.5 In.	0.375 In.
Up to 10	38	53	82	168	168
15	25	35	50	110	168
20		27	40	85	120
25			32	70	90
30				55	75

Note.—Lengths are given for the actual thicknesses indicated. Up to 168 in. the length is limited by the weight of metal available in the standard rolling-ingot. Intermediate thicknesses may be supplied in lengths proportional to those shown in the tables.

TABLE 12.—*Strong Alloy—Flat Sheet*

Width In.	Maximum Lengths, Ft. H Temper					
	Thickness, B. & S. Gage, In.					
	0.250 In.	0.182 In.	0.129 In.	0.064 to 0.032 In.	0.031 to 0.020 In.	0.019 to 0.010 In.
	2 Ga.	5 Ga.	8 Ga.	14–20 Ga.	21–24 Ga.	25–39 Ga.
	Ft.	Ft.	Ft.	Ft.	Ft.	Ft.
¼ to 10.....	18	20	20	20	20	20
Over 10 to 20.....	14	18	20	20	20	20
Over 20 to 25.....	11	15	20	20	20	20
Over 25 to 30.....	9	12	19	20	20	
Over 30 to 35.....	7½	10	16½	20	20	
Over 35 to 40.....	7	9	14	20		
Over 40 to 45.....	6	7½	12	20		
Over 45 to 50.....	4⅔	6½	11	20		

Note.—Lengths given are for the sheet as rolled. At the present time the maximum length of commercial heat-treated flat sheet is 14 ft. in any of the widths listed; for commercial annealed sheet, the maximum length is 15 feet.

Rolled and drawn bar is available in sizes up to 2½ in. in round rod, and up to 1½ in. in squares and hexagons. Larger sizes up to 5 in. can be produced by extrusion. The same limitations as to lengths as were mentioned when discussing extruded shapes apply here also. The tolerances on diameter or distance across flats vary both with the size and with the method of fabrication. Rods and bars which are rolled and then drawn to size have tolerances from ± 0.002 to ± 0.005 in., depending on the size, while rolled bars require a tolerance of ± 0.008 in. Extruded bars may show greater deviations from the nominal diameter, but where the close tolerances are desired, they are given a sizing draw.

TABLE 13.—*Strong Alloy Coiled Sheet (All Tempers)*

Width, In.	Maximum Lengths, Ft.									
	Thickness, B. & S. Gage, In.									
	0.080 In.	0.064 In.	0.050 In.	0.040 In.	0.032 In.	0.025 In.	0.020 In.	0.016 In.	0.013 In.	0.010 In.
	12 Ga.	14 Ga.	16 Ga.	18 Ga.	20 Ga.	22 Ga.	24 Ga.	26 Ga.	28 Ga.	30 Ga.
¼ to 16	Ft. 34	Ft. 34	Ft. 34	Ft. 60	Ft. 75	Ft. 100	Ft. 120	Ft. 150	Ft. 100	Ft. 100
¼ to 12										

CASTING ALLOYS

As was stated previously, "aluminum castings" are, practically without exception, aluminum alloy castings, the alloying elements being added to improve both the mechanical properties and the casting characteristics of the metal. While a great diversity of alloys has been investigated and many of them patented, there is a relatively small number in general commercial use. There are two factors contributing to this result: first, a desire to retain as simple an alloy as possible both from the standpoint of composition control and from a consideration of the utilization and segregation of scrap in the foundry; second, the question of cost of the alloy element restricts the choice to a relatively small number of metals.

In aluminum casting alloys, the increase in tensile strength, yield point and hardness is accompanied by a decrease in elongation and by some sacrifice of corrosion resistance. The extent to which the various properties are affected depends upon the alloying element and upon the amount which is added. In general, the strength increases with increasing percentage of added element up to a certain point, beyond which the only effect is to produce excessive brittleness in the metal. This limiting percentage varies widely with different alloying elements. Moreover, the properties other than strength vary independently, depending upon

the particular alloy composition, that is to say, alloys having the same strength produced by the addition of different elements will, in general, not have the same elongations, yield point, corrosion resistance or foundry characteristics.

The alloying constituents of aluminum are practically confined to the following list: copper, silicon, zinc, manganese, magnesium, nickel and iron; and practically all aluminum base casting alloys are made up by the addition of one or more of these elements.

TYPES OF CASTING PROCESSES

There are three different types of casting processes in commercial use at the present time: sand casting, in which the metal is poured in a mold made of molding sand, the permanent mold process, in which the alloy is poured into a mold made of special heat-treated alloy steel, and die casting, in which the alloy is forced under high pressure into a steel mold. In the permanent mold method, the cores are also made of steel, while in the variation of this process known as the semipermanent mold method, the cores are made of sand.

Each of these processes has its rather definite field of application and its advantages. The latter two processes are applicable only where a large number of identical parts are required, because the cost of the die is high. Where only a small number of castings are to be made or where the casting is very large, the sand-casting process is obligatory. The maximum weight of an aluminum alloy casting poured in a metal mold or pressure die cast, seldom exceeds 20 lb. and weights under 10 lb. are most common.

The use of metal molds permits working to closer tolerances and produces a better surface. Finishing costs, machining and polishing are thus reduced to a minimum; for example, for sand castings tolerances are expressed in eighths and sixteenths of an inch; for permanent mold castings, in thirty-seconds and sixty-fourths; while for die castings, thousandths of an inch are used. For this latter class of material, the finishing may consist merely of removing fins and polishing. The die-casting process is especially suited for castings having thin sections such as meter cases, typewriter frames, carbureters, fire alarm boxes and the like. One of the largest uses of the permanent mold process is in the manufacture of pistons for automobiles.

SAND-CASTING ALLOYS

Table 14 contains a list of the casting alloys in common use in this country, together with their nominal compositions and mechanical properties. A brief discussion of the principal fields of application may be desirable. All of these alloys are available in the form of castings

and practically all, with certain restrictions as regards patent rights, can be purchased in the form of ingot for remelting.

The most commonly used alloys in this country are No.'s 12 and 112, both containing approximately 8 per cent. copper, the latter having in addition small percentages of added iron and zinc. These alloys are readily handled in the foundry and are used wherever a general utility alloy is adequate for the requirements of the service. In fact, the majority of the total tonnage of aluminum alloy castings poured in this country is in these alloys. They are used, for example, in the manufacture of automobile crank cases, oil pans, motor housings, vacuum sweeper parts, etc.

TABLE 14.—*Aluminum Sand-casting Alloys*

[Properties Obtained from Individually Cast Unmachined Sand-cast Test Specimens]

Alloy No.	Approximate Composition, Per Cent.	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation, Percentage in 2 In.	Approximate Yield, Lb. per Sq. In.	Approximate Brinell Hardness No.
100	Aluminum..... 99.0	12,000 to 14,000	15 to 25	4,000	25
12	Copper..... 8.0	18,000 to 23,000	1 to 3	10,000	65
112	Copper..... 7.5	19,000 to 24,000	1 to 2.5	11,000	65 (Minimum 60)
	Zinc..... 1.5				
	Iron..... 1.2				
109	Copper..... 12.0	20,000 to 28,000	0 to 1.5	15,000	70
43	Silicon..... 5.0	17,000 to 22,000	3 to 7	7,000	40
45	Silicon..... 10.0	17,000 to 21,000	1.5 to 3	9,000	50
*47	Silicon..... 13.0	24,000 to 31,000	5 to 15		
	(Modified)				
*195	Copper 4.0 HTT No. 4.....	28,000 to 38,000	6 to 12	13,500	65 (Minimum 50)
*195	Copper 4.0 HTT No. 16.....	30,000 to 40,000	3 to 8	21,000	75 (Minimum 70)
*195	Copper 4.0 HTT No. 10.....	36,000 to 50,000	0 to 5	27,000	100 (Minimum 80)
*196	Copper..... 5.0	33,000 to 45,000	0 to 2.5	27,000	110
	HTT				
*145	Zinc..... 10.0	25,000 to 37,000	3 to 6	12,000	65
	Copper..... 2.5				
	Iron..... 1.2				
*122	Copper..... 10.0	35,000 to 40,000	0 to 1.0	20,000	115
	Iron..... 1.2				
	Magnesium..... 0.25				
	HTT 10				
"Y"	Copper..... 4.0	30,000 to 40,000	0.5 to 2.0	25,000	100 Minimum
or	Nickel..... 2.0				
142	Magnesium..... 1.5				
	HTT				

* The modification process by means of which the properties specified for No. 47 alloy are realized, the production of castings of alloys Nos. 122, 195 and 196 in the heat-treated state, and alloy No. 145 are covered by patents or patent applications owned by Aluminum Co. of America.

Where the castings must be leak-proof or pressure-tight, these alloys are not suitable. For such service, the copper is raised to around 13 per cent. This alloy, listed as No. 109, has less shock resistance than those containing less copper and consequently, it is not suitable for use where

it is subjected to severe impact stresses. It is used for automobile motor manifolds, pump parts and the like.

By using a copper content of about 9 per cent., adding a small amount of magnesium and increasing the iron somewhat, the alloy listed as No. 122 is obtained. This material is used in making castings which are subject to wear, such as valve guides, cam shaft bearings, etc. This

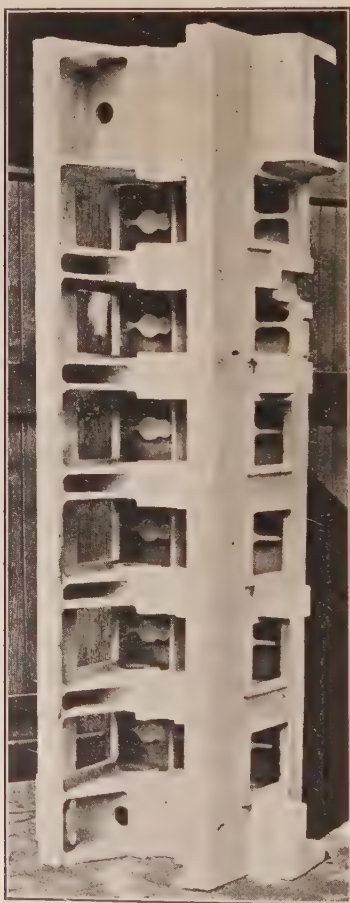


FIG. 2.—HEAT-TREATED ALUMINUM ALLOY CASTING. AUTOMOBILE CRANK CASE
No. 195 ALLOY, WEIGHT 668 LB.

alloy is also used in permanent molds for the manufacture of pistons; for this purpose the castings are usually heat-treated to further improve the hardness.

The alloy No. 195, having around 4 to 5 per cent. copper with permissible additions of very small percentages of magnesium and zinc, is of interest because of the exceptional properties which are obtained by heat

treatment. While it is true that the working of an alloy very greatly increases its capacity for responding to heat-treatment processes, the impression which was current some years ago based on ineffectual attempts to produce heat-treated castings, that cast aluminum alloys could not be effectively heat-treated, is obviously not correct. Another misapprehension which must be corrected is the belief that only small simple castings can be heat-treated. Several large complicated castings are in regular commercial production; one of these, a large fire engine crank case, weighs over 650 lb. (Fig. 2). It is necessary to design the pattern in accordance with the characteristics of the alloy, the principal feature being the use of fillets rather than sharp angles between heavy and light sections. However, this alloy is strictly a commercial alloy. While its tonnage does not compare with that of No. 12 and No. 112 alloy, just as the production of steel castings does not compare with that of ordinary cast iron, it is, nevertheless, being used in ever-increasing amounts where special quality castings are desired.

EFFECT OF HEAT TREATMENT ON STRENGTH

Castings are supplied in three different heat treatments. Heat treatment 4 gives very good strength combined with a high elongation; by a modification of the heat-treating practice somewhat higher strength and a much higher yield point are obtained but approximately half of the elongation is sacrificed. By a still further change in the heat treatment, quite extraordinary strengths are obtained but little elongation is retained. The choice between these products will be determined by the nature of the service to be performed; where maximum shock resistance is required, the higher elongation will naturally be chosen.

It should be mentioned that in alloy No. 195-HT4, there is some aging of the metal at ordinary temperatures; after a period of several weeks the tensile strength will show a small increase and the elongation, a slight decrease, but the yield point may increase by as much as 50 per cent. No. 196 alloy permits the development of higher Brinell hardness than is obtained with 195 alloy, and where this property is of importance its use is indicated.

SILICON ALLOYS

The silicon alloys are a more recent development, but they have found a field in the casting industry. These alloys are the most resistant to salt water and various other types of corrosion of all the common casting alloys. The alloy containing 2 per cent. of manganese, which is sometimes used for the manufacture of pipe fittings and other small castings, alone is comparable with them. They all form dense, pressure-tight castings; and in addition, they have good casting qualities, permitting the pouring of intricate castings having both thin and heavy sections, with

remarkable ease. They require some care in remelting since they have considerable tendency to pick up iron from the remelting equipment if it is not properly protected, and this element is objectionable in these alloys from the standpoint of lowering the elongation. These alloys do have the shortcoming of a relatively low yield point in comparison to their ultimate tensile strength. The specific gravities of these alloys are lower than that of pure aluminum.

The alloy containing 5 per cent. silicon, No. 43, is perhaps the most widely used in this country, although it finds less favor abroad. This alloy has somewhat lower strength than the copper alloys No. 12 and No. 112 but it has a distinctly higher elongation. Because of its excellent casting characteristics, it finds quite extensive use; it has also replaced alloy No. 109 for many purposes since it combines excellent shock resistance with the required pressure tightness. The 10 per cent. alloy, No. 45, has slightly higher strength but lower elongation, which latter fact appears to have prevented a more widespread use.

The use of No. 47 alloy containing 13 per cent. silicon, in sand castings necessitates the use of one of the patented modification processes if desirable mechanical properties are to be obtained. When cast in sand without such modification, the strength is much lower than the values shown in the table and the alloy breaks with a coarsely crystalline brittle fracture, in marked contrast to the fine silky fracture of the modified alloy. This alloy is quite extensively used in Germany where it is sold under the name "Silumin," in France and in this country the name "Alpax" is used. In this country, the development has not been so great, due in part, no doubt, to the extensive use of No. 195 alloy in the field of quality castings.

ZINC, COPPER AND IRON-ALUMINUM ALLOYS

No. 145 alloy is an alloy of zinc, copper and iron with aluminum, which has quite interesting properties. It differs from the alloy L5, which in England occupies a position similar to that held by No. 12 in this country, in having a lower zinc content and in containing added iron. This alloy has higher tensile properties than those of the ordinary casting alloys and greater shock resistance; it stands intermediate between these alloys and the heat-treated castings. This alloy does not retain its strength at elevated temperatures so well as do the aluminum copper alloys and it is not recommended for high temperature service.

The alloy developed in the National Physical Laboratory in England under the name "Y" alloy and sold in this country both under this name and under the designation No. 142 alloy is especially intended for use at elevated temperatures. This alloy is used to some extent for pistons for aircraft motors and for Diesel engines; it is capable of improve-

ment by heat treatment, the tensile strength being comparable with that of 195 alloy but the elongation is much lower.

Aluminum alloy castings find their most extensive use where it is desired to keep weight at a minimum, usually for the purpose of conserving power; motors for aircraft, automobiles, trucks, buses, small boats and the like, are outstanding examples. So far as is known, the largest

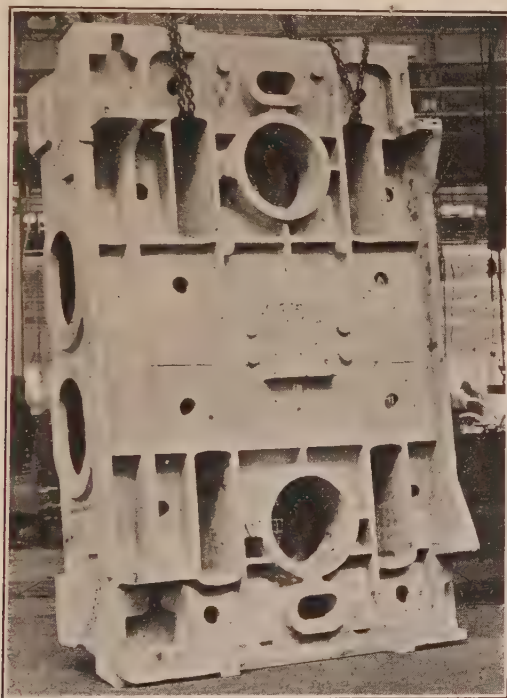


FIG. 3.—ALUMINUM ALLOY CASTING. DIESEL ENGINE BASE WEIGHING 3800 LB.

complicated cored casting which has ever been poured in the light alloys was a Diesel engine base weighing 3800 lb., for installation on a yacht (Fig. 3). Not infrequently, however, other considerations also influence the choice of aluminum. The ease of machining and of polishing to produce a pleasing enduring finish accounts for a considerable tonnage of aluminum alloy castings as well as forgings.

PERMANENT MOLD CASTINGS

Some of the alloys used in making sand castings are also poured in permanent molds; others have been developed primarily because of their suitability for this process. The alloys, when poured in chill molds, have a finer grain structure because of the more rapid solidification of the metal,

with the result that chill-cast test specimens show higher tensile properties than do the bars cast in sand from the same alloy. Whether this same difference in strength will be maintained in the actual castings made by the two processes depends upon the nature of the casting and the ability to design the metal mold to retain the advantage which is inherent in the chill process.

In this connection, it should be noted that the alloys high in silicon, when cast in chill molds, develop a structure and properties similar to those obtained by the modification process when the alloy is cast in sand. This use of the alloys containing added silicon for the manufacture of chill castings is covered by patents owned by the Aluminum Co. of America.

TABLE 15.—*Permanent-mold-cast Alloys*
[Standard 0.505-in. Test Specimen, Cast in Permanent Mold]

Alloy No.	Approximate Composition, Per Cent.	Tensile Strength, Lb. per Sq. In.		Elongation, Percentage in 2 In.		Brinell Hardness No.
43	Silicon..... 5.0	18,500	24,500	3.0	8.0	40 to 45
108	{ Copper..... 4.5 Silicon..... 5.5 }	21,000	29,500	1.0	4.5	65 to 80
45	Silicon..... 10.0	24,500	29,500	4.5	10.0	45 to 56
112	Same as sand-cast. 112 (as cast)	21,000	29,000	1.5	3.0	70 to 90
122	{ Copper..... 10.0 Iron..... 1.2 Magnesium..... 0.25 }	22,000	30,000	0.0	1.5	85 to 105
125	{ Silicon..... 5.0 Iron..... 1.0 Tin..... 2.0 }	17,500	22,500	4.3	8.0	40 to 45
151	{ Copper..... 5.5 Iron..... 1.0 Tin..... 1.0 }	20,500	26,500	3.5	7.5	60 to 70
152	Copper..... 10.0	20,500	29,500	1.0	3.0	85 to 110
195	Copper..... 5.5	22,000	28,000	3.0	6.0	60 to 70

Heat-treated Alloys

	Heat-treat No.					
195	4	35,000	39,000	5.0	9.0	70 to 90
195	10	48,000	54,500	1.0	1.5	110 to 140
122	2	24,000	30,000	0.5	1.5	90 to 120
122	7	40,000	48,000	0.5	1.0	125 to 160
122	12	24,500	32,500	0.5	1.0	125 to 160
122	14	24,000	30,500	0.5	2.0	95 to 125
122	15	26,000	32,500	0.5	1.5	115 to 125

The outstanding advantages of this process, namely: close tolerances and ease of finishing, have already been discussed; and enumeration of some few of the castings which are in commercial production may be of

interest: pistons have already been mentioned, automobile brake shoes, ironing machine shoes, small gear wheels, heavy cooking utensils, machinery parts, etc. The alloy used will depend both upon the service conditions and upon the foundry requirements for the particular part. Some of the more commonly used alloys are shown in Table 15.

DIE CASTINGS

A considerable range of alloy compositions is in use for the manufacture of die castings by the various manufacturers. The choice of alloy is determined to a considerable extent by the character of the die-casting machines and the operating practices and by the requirements of the given part from the standpoint of production. There is, in addition, the question of mechanical properties necessary for the part to meet the



FIG. 4.—DIE CASTING. ONE OF THE LARGEST, ALTHOUGH NOT HEAVIEST, DIE CASTINGS IN COMMERCIAL PRODUCTION. WEIGHT 6.2 LB., BASE DIMENSIONS $9\frac{1}{4}$ BY $12\frac{1}{4}$ IN.

(Principal part of a tilted tub washing machine and centrifugal drying machine.)

conditions under which it is used. The question of the properties of the various alloys is now in process of a thorough investigation by cooperative tests sponsored by a committee of the American Society for Testing Materials, in which both producers and consumers are participating.

Typical examples of die castings in production are adding machine frames, carbureters and other automotive accessories, radio loud speaker

standards and frames, meter cases, brake shoes, novelties of one sort or another, etc. (Fig. 4.). The principal consideration is the reduction of production and finishing costs. In some cases, bushings or inserts of other metals to resist wear may be cast in place.

While the term "pressure die casting" may convey the impression of exceptional soundness of the metal, it must be borne in mind that in this process there is little or no opportunity for the feeding of the casting because of the rapidity with which the alloy freezes; there must, therefore, be a certain amount of porosity in the interior of the metal. Die castings must be judged, therefore, on their ability to meet service requirements, rather than on a critical inspection of fractured surfaces.

ALUMINUM ALLOY FORGINGS

One of the growing applications of the strong aluminum alloys is in the manufacture of forgings. As has been stated previously, 25S alloy, 51S alloy and duralumin are most commonly used alloys for this purpose.

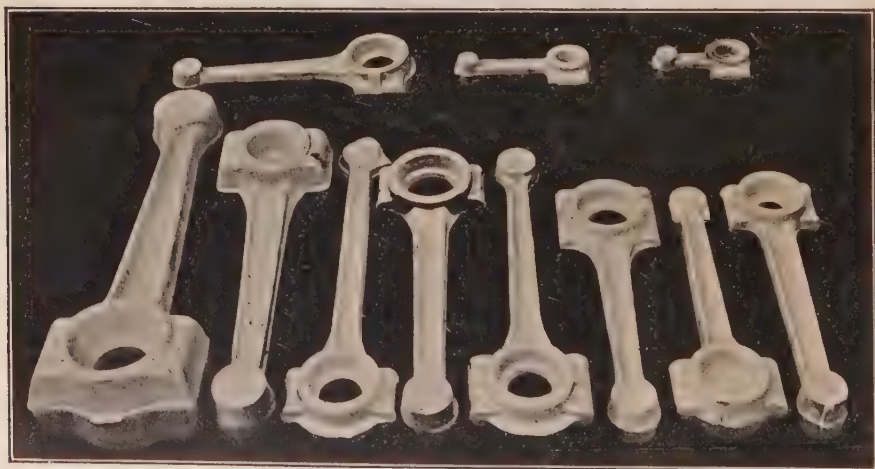


FIG. 5.—ALUMINUM FORGINGS. CONNECTING RODS MADE FROM 25S ALLOY.

The manufacture of automobile connecting rods, propellers for aircraft, and automobile hardware consumes a considerable tonnage of these alloys (Fig. 5). One of the well known aeroplane engines of the radial type uses a forged crank case. Various reciprocating machinery parts are being made as aluminum alloy forgings in order to take advantage of the reduction in weight with the consequent reduction of inertia stresses. This list of uses, while in no wise complete, will serve to indicate some of the possibilities of these products.

SPECIAL PRODUCTS

There are various fabricated products of aluminum or aluminum alloy which are regular articles of trade. Automatic screw machine products in a wide variety of forms are manufactured from 17ST alloy and duralumin; wood screws, machine screws, stove bolts, bolts and similar parts are available in the range of standard sizes and threads.

Rivets in 2S and 17S or duralumin are standard commercial products. Corrugated sheet for roofing or building construction, special design aluminum shingles and roofing nails of 17ST alloy are a fairly recent development. Aluminum furniture is now being produced on a commercial scale and combines with the recognized advantages of metal furniture the further advantage of lightness.

Aluminum bronze powder is becoming a widely used paint pigment because of its durability and its excellent protective action on both steel and wood, its high reflectivity for light and heat rays and its remarkable covering power. This use of aluminum is mentioned because of the increasing tonnage of the metal which is used for this purpose, even though it is not a metallurgical application.

Probably the most recent development is the introduction of "Alclad" strong alloy sheet. This is a product consisting of a core of the strong alloy and a surface layer of aluminum of very high purity alloyed and integral with the core. The thickness of the surface layer is so chosen as to afford the exceptional corrosion resistance of aluminum of high purity and, at the same time, retain the maximum possible mechanical properties in the sheet. This development is so new that it is not yet possible to predict the extent to which it may be carried. Alclad 17S sheet is now in commercial production and it is contemplated that other alloys will also be marketed in the "Alclad" form.

ALUMINUM CABLE

Aluminum cable for use in power transmission has been in regular production for a number of years and consumes a large tonnage of the metal. For some purposes the cable consists entirely of aluminum wires, but more commonly the aluminum wires are stranded around a core made up of galvanized steel wires having a high tensile strength and yield point. The conductivity is all calculated on the basis of the aluminum strands, the steel serving merely to increase the tensile properties of the composite cable.

Although aluminum of the grade used in the manufacture of cable has a specific conductivity of only 61 per cent. of the annealed copper standard, the low specific gravity of the metal again enters, and pound for pound, it will carry practically double the current of a copper conductor. This same weight, conductance ratio is, of course, not maintained in the

composite steel reinforced cable. The aluminum conductor is naturally larger in diameter than the copper cable designed to carry the same current, which fact is advantageous in high voltage power transmission due to lessening of corona losses.

One of the advantages of the steel-reinforced aluminum cable is its high ratio of strength to weight, which permits the use of long spans. Except for one instance where an all-steel cable was used, the longest span in the world is in one of the power lines of the Southern California Edison Co., the distance between supports being 5190 ft., a little less than a mile.

This paper, prepared in response to the request of the committee in charge of this symposium, is presented with the hope that it may give a more general idea of the commercial side of the aluminum industry as it exists today. Developments now in progress, it is expected will change in the near future some of the statements which have been made, particularly as to limiting commercial sizes, tolerances and even mechanical properties. Some of these have been suggested, but the aim has been to state what can be obtained on the market today. No attempt has been made to cover any of the metallurgical considerations; the one purpose has been to answer the question: "What is the present status of aluminum and aluminum alloy products in the United States?"

Some Aspects of the Commercial Manipulation of Aluminum

By C. F. NAGEL, JR.,* NEW KENSINGTON, PA.

(Detroit Meeting, September, 1927)

THIS paper is written primarily for those who are familiar with the processes mentioned but who desire a further insight into some of the fundamental principles. It does not give a complete description of the various practices employed in the working of aluminum and its alloys, but presents a few illustrations of the essential respects in which aluminum differs from other common metals, and emphasizes the controlling factors of the processes under consideration.

HEAT TREATING

Certain aluminum alloys are capable of having their mechanical properties greatly altered by a heat-treatment process. The degree of this improvement may be illustrated by some typical properties of duralumin (Table 1). It is essential that the material be in the wrought condition in order to obtain maximum heat-treatment effects.

TABLE 1.—*Typical Properties of Duralumin*

	Annealed	Heat Treated
Tensile strength, lb. per sq. in.....	28,000	59,000
Yield point, lb. per sq. in.....	9,000	34,000
Elongation, percentage in 2 in.....	18	18
Brinell hardness (500 kg.—10 mm. ball).....	50	95

In the case of duralumin, the process consists of heating the metal to a prescribed temperature and then quenching it. Immediately after quenching, the material is relatively soft though not as soft as in the annealed state. If allowed to stand at room temperature, the material changes, increasing in hardness and strength without loss of elongation, but at the expense of the plasticity. This action is very rapid at first, gradually diminishing in intensity and to all practical purposes being completed in about four days. This process of hardening is termed

* Assistant Technical Director, Aluminum Co. of America.

"aging." The change in properties during this aging is illustrated by the data of Table 2.

TABLE 2.—*Change in Properties of Duralumin during Aging*
17S Sheet 0.064 in., Quenched from 940°–950° F., Aged at Room Temperature

Aging Time	Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Elongation, Percentage in 2 In.
1 hour	44,830	21,150	19.0
1 day	54,755	32,350	18.7
2 days	56,115	33,000	18.7
6 days	56,765	34,850	19.7
10 days	57,175	34,350	19.7

The aging process will be slightly accelerated by quenching in boiling water instead of in cold water, though the ultimate properties will be about the same.

Certain alloys age spontaneously at room temperature while others require a second heating after the first heating and quenching in order to produce this effect. When the material must be heated to produce this aging, the process is termed "artificial aging."

TABLE 3.—*Mechanical Properties Characteristic of Certain Alloys in Various Tempers*

Material	Condition	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg.— 10 Mm. Ball
		Lb. per Sq. In.			
17ST	Quenched and aged at room temperature.....	30,000 to 40,000	55,000 to 63,000	18 to 25	90 to 105
17SO	Annealed.....	7,000 to 12,000	25,000 to 35,000	14 to 22	45 to 55
25SO	Annealed.....	7,000 to 12,000	23,000 to 35,000	14 to 22	45 to 55
25SW	Quenched and aged at room temperature.....	15,000 to 30,000	45,000 to 53,000	15 to 22	68 to 85
25ST	Quenched and aged at ele- vated temperatures	30,000 to 40,000	55,000 to 63,000	16 to 25	95 to 105
51SO	Annealed.....	4,000 to 6,000	14,000 to 19,000	22 to 32	25 to 32
51SW	Quenched and aged at room temperature.....	15,000 to 20,000	30,000 to 40,000	20 to 30	55 to 70
51ST	Quenched and aged at ele- vated temperatures	30,000 to 40,000	45,000 to 50,000	10 to 18	90 to 100
A-17SO	Annealed.....		20,000 to 25,000	20 to 28	30 to 40
A-17ST	Quenched and aged at room temperature.....	15,000 to 20,000	35,000 to 45,000	20 to 28	55 to 75
B-17SO	Annealed.....		20,000 to 25,000	20 to 28	30 to 40
B-17ST	Quenched and aged at room temperature.....	20,000 to 25,000	42,000 to 50,000	20 to 28	65 to 85
Special 17SO	Annealed.....	7,000 to 10,000	25,000 to 35,000	12 to 20	42 to 55
Special 17SW	Quenched and aged at room temperature.....	30,000 to 40,000	55,000 to 63,000	18 to 25	90 to 105
Special 7 ST	Quenched and aged at ele- vated temperatures	50,000 to 55,000	63,000 to 70,000	8 to 14	95 to 125

The complete heat treating of these alloys may be divided, therefore, into two stages:

1. Solution heat treatment, the object of which is to bring the soluble constituents into solid solution and to retain them in a supersaturated state by rapid cooling.

2. Precipitation heat treatment, termed "aging," during which the soluble constituents in solution in excess of that required by equilibrium are precipitated in a finely divided and critically dispersed state.

It follows from this that alloys which only age spontaneously at room temperature can be supplied to the trade in only one heat-treated temper, namely, the fully heat-treated and aged state,[†] while alloys susceptible to artificial aging can be supplied in two heat-treated states; (1) heat-treated and quenched but not artificially aged, and (2) heat-treated, quenched, and artificially aged. An example of the latter case is the 25S alloy mentioned later, which is supplied in two heat-treated tempers—25SW and 25ST. The first has not been artificially aged while the second has received this treatment.

Table 3 gives the mechanical properties listed by the manufacturer as characteristic of certain alloys in various tempers.

All the alloys in this list except the 25S age harden to some extent at room temperature and hence are more plastic immediately after quenching than a few days later. The properties noted are those for the four-days room-aged condition. 25SW has the properties noted promptly after quenching.

Solution Heat Treatment

The heating may be done either in air or by immersing the material in a molten bath of nitrate, which may consist of a mixture of sodium and potassium nitrates or may be merely a commercial grade of sodium nitrate. The material should be heated to the temperatures prescribed in Table 4 and held there for a sufficient length of time to permit solution of the soluble constituents. This time will vary with the amount of metal in the furnace, the thickness of the material, and the amount of mechanical working it has received. For material that may be classified as sheet, 15 to 30 min. is sufficient, the thinner sheet requiring the shorter time. In the case of heavy bars and slabs, several hours may be necessary. This time refers to the period at temperature and does not take into account the time required to heat up the material. It is obvious that a longer time will be necessary to bring the material to temperature in heated air than in a molten liquid.

Accurate temperature control is essential. The heat-treatment effects increase gradually with rise in temperature until the maximum solution of soluble constituents has been attained. If the heat-treating temperature is too low, only partial effects will be obtained, while if the temperature is too high, partial melting and "burning" of the alloy will

take place, with consequent loss of ductility and strength. Badly burned material is characterized by a slightly wrinkled or blistered surface, a crystalline fracture, and fused areas noted in the microstructure. It is difficult to detect "burning" in its earlier stages, hence the need to avoid approaching "burning" temperatures. The temperatures recommended in Table 4 are sufficiently below the burning temperatures of the respective alloys so that the practice may be safely carried on without danger if reasonable precautions are exercised.

TABLE 4.—*Temperatures Required for Solution Heat Treatment*

ALLOY	TEMPERATURE, DEG. FAHRENHEIT
Duralumin, 17S, A-17S, B-17S.....	940 to 960
25S and 51S.....	960 to 980
Special 17S.....	920 to 930

When the material has been at temperature the required length of time, it should be removed and quenched. The initial rate of drop in temperature should be as rapid as possible, hence the least possible time should be lost in transferring the metal from the heating chamber to the quenching medium.

Quenching may be done by plunging into hot or cold water or oil, or by playing an air blast on the material. Thin sheet (0.020 in.) will quench in still air with sufficient rapidity to give very substantial heat-treating effects. Maximum effects can be obtained with increase in rate of quenching. The resistance to corrosion is affected to a greater extent by rate of quenching than are the mechanical properties. For example, practically identical properties are obtained by quenching very thin sheet either in air or water, though the material quenched in water shows a greater resistance to corrosion.

Both the act of heating and of quenching, especially the latter, may cause some warping. As the material is relatively soft immediately after quenching, it is easiest to straighten the metal at that time.

The heating furnace may be either an air chamber, heated preferably by electricity, as this permits of very accurate control, or a nitrate tank heated by gas. No detailed description can be given for an electrically heated air furnace because this will depend so much on the character of the work to be handled. The essential features call for uniform temperature throughout the heating chamber and a means of accurately controlling the temperature. It is recommended that automatic controllers and recorders be used on such furnaces. The nitrate-tank furnace consists simply of a sheet-steel or cast-iron tank of suitable dimensions for the particular work at hand, heated from the outside, preferably by gas. It is desirable to have the hot gases play around both the sides and the bottom of the tank. In order to insure uniform temperatures throughout the bath, in the case of long rectangular tanks, a number of burners should be placed along the sides rather than merely one large burner. Though it

is relatively easy to control the temperature of such a bath, pyrometers are absolutely essential and it is best to have these constantly in the bath.

When heating a large number of items at one time, such as a pack of sheet, the pieces should be separated by spacers and the nitrate should be circulated so as to introduce hot nitrate into the central portion of the load where the salt has been chilled and entrapped by the cold metal. Difficulties of this nature may be overcome by slowly jiggling the load vertically during the time that it is suspended in the nitrate.

Prior to immersing, it is good practice to suspend the load just above the molten bath a few minutes to be sure that no moisture is present at the time of immersion to cause dangerous spattering of molten nitrate.

After quenching from a nitrate bath, it is important that all the salt be completely removed; otherwise, on standing in a moist condition, the nitrate may have a corrosive effect on the alloy. It is recommended, therefore, that a second rinsing tank be provided in addition to the quenching tank. When heat treating continuously, there should be a constant flow of clean water through this rinsing tank. Quenching in hot water facilitates the removal of nitrate.

The quenching tank should be sufficiently close to the heating chamber to permit of quick transfer from one to the other. When large numbers of items are to be treated, these can be handled easily by placing them in a steel frame or expanded metal basket hung from an overhead trolley or jib.

Although nitrate baths are used in various industries, attention should be given to the fact that the fused salt coming in contact with carbonaceous or organic material, such as wood, coke, etc., or red-hot iron or steel, may be the cause of an explosion. Therefore, in the designing of such a furnace, the flame should not be permitted to blast directly on the iron or steel container. Extra sacks of nitrate should be stored in a dry place and at a distance from the tank. When adding fresh nitrate to the tank, the operator should see that it is perfectly dry. In the case of a nitrate fire, do not use water. Dry sand is recommended to put out such fires, and a supply of dry sand should be kept on hand for this purpose.

It is not intended to convey the idea that the hazards of nitrate heat treating are so great as to make it inadvisable to employ this method. The precautions are mentioned merely in order to avoid difficulties.

Precipitation Heat Treatment

The times and temperatures prescribed for alloys 25S, 51S and Special 17S are shown in Table 5. Other alloys may require somewhat different combinations of time and temperature, which will have to be determined by experimentation. The best temperatures lie between 250° and 320° F. As a general rule, longer times are required with lower temperature, though, on the other hand, more desirable combinations of tensile strength and elongation can be obtained by employing longer

times at lower temperatures. In order to duplicate results, it is essential to accurately control time and temperature. Here, as in the case of the solution heat treatment, the times and temperatures given apply to the period at heat and do not include the time required to bring the material up to temperature.

Any chamber in which uniform temperatures can be obtained and accurately controlled will be suitable for conducting the artificial aging treatment. Live steam may be used as the heating medium in the case of heavy sections such as large forgings. Aging of thin sheet alloys should not be conducted in live steam, however, as steam has some action on the surface of the alloys, especially if the solution heat treatment has been carried out in nitrate. The chamber may be heated by steam coils. Whatever system is used, the temperature should be uniform throughout the chamber. It is usually necessary to provide some means of artificially circulating the atmosphere. This can be accomplished by providing fans in the ceiling, with baffles so arranged that the fans will draw air from the bottom of the furnace.

TABLE 5.—*Times and Temperatures for Precipitation Heat Treatment*

ALLOY	TEMPERATURE DEG. F.	TIME HR.
25S.....	285 to 295	8 to 15
51S	310 to 320	18
Special 17S }		

The operating technique is extremely easy and simple as control of rate of heating and cooling is not required, it being only necessary to place the material in the chamber and leave it there the prescribed time. As no distortion difficulties are encountered, the handling problem is comparatively simple. The main essential is to space the individual pieces in each load so as to assist in equal heating of all items.

ANNEALING

The usual object of annealing aluminum and its alloys is to remove the strain-hardening imposed by previous cold working. Space does not permit any complete or thorough discussion of the theories and principles involved but a few points will be useful in understanding the reasons for selecting certain operating practices.

When a metal is cold worked, the deformation puts the material in individual crystals under strain and may cause a non-uniform orientation of atoms within a crystal. Heat will permit the release of these strains and a re-orientation of the atoms. This is termed "recrystallization." The recrystallization temperature will be different for different metals and will also vary among crystals in the same piece of metal. This temperature will usually be lowered with:

1. Increase in time at elevated temperature.
2. Increase in purity of metal.

3. Decrease in temperature at which deformation took place.
4. Decrease in size of original grain.
5. Increase in amount of strain-hardening.

Though the effect of some of these factors upon the recrystallization temperature may be very great, it is impractical in commercial practice to operate at the lowest theoretical recrystallization temperature of each piece of metal. For example, it would not be feasible, or generally useful, to heat only to 450° F. rather than 650° F. when the lower temperature may require a period of 6 days at heat as compared to 2 min. at the higher temperature. Neither is it possible, with our present knowledge, to predict, as an operating procedure, the minimum recrystallization temperature and, furthermore, this temperature will vary from crystal to crystal in the same piece of metal. Hence, in the commercial annealing of aluminum a temperature is selected, as determined by experience, for each alloy, at which recrystallization will be complete for all expected conditions of the metal. This is termed the "annealing temperature," the values commonly used are given in Table 6.

TABLE 6.—*Annealing Temperatures for Aluminum and Alloys*

Trade Designation	Material					Annealing Temperature
	Al, Per Cent.	Cu, Per Cent.	Mg, Per Cent.	Mn, Per Cent.	Si, Per Cent.	
2S.....	99					650° F.
Duralumin						
17S.....	Min. 92.0	3.5-4.5	0.3-0.75	0.4-1.0		650° F.
25S.....	Min. 92.0	3.9-5.0	0.5-1.1		0.5-1.1	650° F.
51S.....	Min. 95.5		0.45-0.80		0.60-1.20	650° F.
3S.....	Min. 97.1			1.0-1.5		800° F.

For all practical purposes, recrystallization is instantaneous at these temperatures. It is sufficient merely to raise the metal to these values; it is not necessary or generally desirable to hold it there for any considerable time.

When strain-hardened wrought aluminum is heated beyond its recrystallization temperature, some crystals in the recrystallized metal immediately begin to grow at the expense of surrounding material. Under suitable conditions a product will result in which individual crystals may be over an inch long. In general, a coarse crystal structure is not as desirable as a fine one because such metal is weaker and will not successfully take the same deformation. Furthermore, when forming the metal, as in a drawing operation, a rough surface will result which will require extra labor to first grind it smooth if the article is to be polished.

Though ultimate crystal size is influenced and may be governed by conditions other than those occurring during annealing, considerable

control may be exercised by choice of suitable annealing practices. Therefore it is useful to know the conditions conducive to crystal growth and those annealing methods which, if followed, will tend to produce a small crystal size.

There is considerable reason to believe that a growing crystal can acquire material from adjacent unrecrystallized metal more easily than it can from recrystallized metal. This process of a growing crystal feeding upon neighboring material involves the element of time. When a piece of fully annealed metal is cold worked all the crystals are not strained to an equal degree. During the annealing operation, the crystals that have been subjected to the greatest strain will be the first to recrystallize and can commence to grow at the expense of the adjacent unrecrystallized material. If then, the rate of heating is so slow that the recrystallization temperature of the least strained material is never reached, or reached only after a considerable time, such material may be entirely absorbed by the growing crystal.

There is, therefore a critical amount of strain-hardening that is most conducive to crystal growth. The annealing of a partly formed article, such as a drawn shell, thus presents some difficulty because the strain-hardening in the metal will vary greatly, a certain area of it almost inevitably having this critical amount. The critical stage is reached early and corresponds to only a few per cent. reduction in thickness as produced by a rolling operation.

Having these principles in mind, the practice to be employed in order to prevent crystal growth will be obvious. Heat the metal as quickly as possible to above the recrystallization temperature of the least strained material (see Table 6). As soon as the metal has reached this temperature, remove it from the furnace, because as soon as recrystallization has occurred crystal growth will commence.

Time and temperature are the two most important technical factors in the correct annealing of aluminum and its alloys. Consideration should be given not only to the temperature of the atmosphere within the furnace, but, equally important, to the temperature of the metal. Therefore it is good practice to employ two thermocouples; one by which the temperature of the furnace atmosphere may be controlled, the other embedded in the coldest part of the load, to tell when the load should be removed. Using two couples, it is possible to operate the furnace at temperatures 150° to 250° F. above the annealing temperatures of the metal, thus employing the desired action of heating the metal more rapidly than could be done were the furnace temperature only slightly above the annealing temperature. Should annealing be carried out by immersing the metal in a liquid bath such as molten nitrate or lead, the temperatures of the bath should be only a few degrees above the recrystallization temperature.

Some thought and care must be given to stacking the load so as to facilitate quick and uniform distribution of heat throughout the mass in order that the metal may be heated quickly.

Annealing of aluminum is made easy by the fact that the metal is not adversely affected by furnace gases. It is not necessary to employ retorts or covers; the aluminum may be placed directly on racks or bottoms and placed uncovered in the furnace.

Occasionally one may be obliged to anneal a section of work. The usual practice is to play a low-temperature flame upon this area. Though this is obviously risky, due to the impossibility of noting the temperature of aluminum by any color change, sections $\frac{1}{8}$ in. thick or greater can be handled in this manner by experienced operators. A two-point pyrometer may be used to show the temperature of the metal. A less accurate indication is to rub the metal with a pine stick. When the metal reaches the temperature of about 800° F., a pine stick will leave a charred mark.

The annealing of heat-treatable aluminum alloys demands additional consideration. As has been previously pointed out, slight heat-treatment effects will be obtained by quenching the metal from only a little above the annealing temperature. Therefore, when annealing such alloys, great care should be exercised not to overheat the metal and, furthermore, in order to assist in wiping out the effects of slight overheating, the metal should be cooled very slowly to below 500° F. If the temperature has not exceeded 675° F., such slow cooling is not essential but if maximum softness is wanted, it is desirable to cool the metal slowly.

Frequently there may be occasion to anneal material that is in the heat-treated state. This demands a special practice which consists of heating the metal for at least one hour at 800° F., and then cooling very slowly to below 500° F. The longer the time at 800° F., and the slower the cooling, the more thoroughly will the material be annealed, as the maximum softness is attained when the soluble constituents are precipitated from solid solution as completely as possible in the form of large particles. To accomplish this requires time and hence the need for cooling slowly.

COLD FORMING

Pure aluminum and the less complex alloys are more plastic than steel or brass in the sense that they will accept a greater deformation without fracturing, and hence can be given a greater number of successive draws without requiring intermediate annealing.

The workability of any metal is, of course, limited by its mechanical properties, and different tempers of the same alloy will have different degrees of ductility. However, there is one property of aluminum and its alloys which introduces certain limitations and requirements. When

planning the cold forming of aluminum, in comparison to the conditions selected for other metals, the most important characteristic to bear in mind is the coefficient of friction. Aluminum has a higher coefficient of friction than brass or steel. The manner in which this property functions may be shown by the following discussion of the drawing of a simple shell.

In Fig. 1, sketch *A*, the cross-hatched portion represents the cross-section of a circle to be formed into the cup shown in sketch *C*; *a* is the die; *b* is the punch. In sketch *B*, we see the punch forcing the sheet circle into the die and in sketch *C* the end of the stroke with the shell formed.

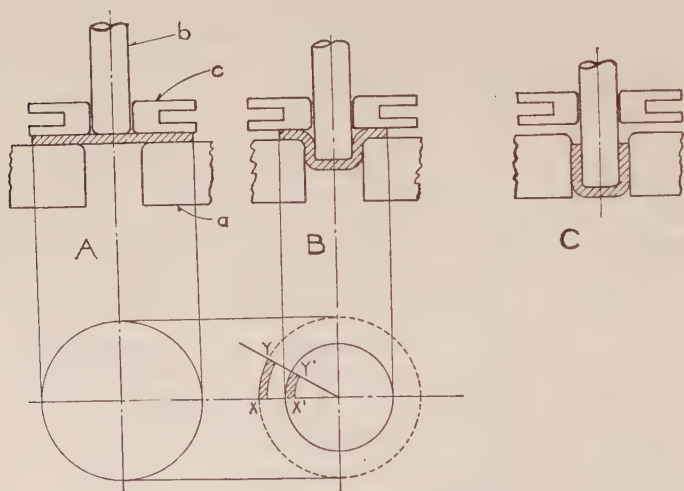


FIG. 1.—COLD FORMING AN ALUMINUM SHELL.

As the punch moves downward, the circumference of the circle must decrease and the arc XY will decrease to the new dimension $X'Y'$. It is obvious that the metal during this movement is put into compression and these compressive forces will tend to relieve themselves by a buckling of the sheet. If the sheet were buckled at the instant that it must move over the die radius, considerable resistance would be set up and, if the buckling were very severe, the resistance would probably exceed the tensile strength of the material and the sheet would break. To avoid such an occurrence, it is necessary to prevent the sheet from buckling. This is accomplished by means of a flat ring *c*, termed the blank holder, which precedes the punch in its downward movement and clamps the sheet circle between this ring and the die. During drawing, the sheet slides between the blank holder and the die. As the compressive forces set up in the circle are large, the tendency to buckle is great, hence con-

siderable pressure must be exerted by this ring against the sheet to prevent buckling. This pressure introduces frictional resistance against the movement of the sheet circle. Precautions must be taken to reduce this resistance to the minimum. With this object in mind, the contact surfaces of the die and blank holder must be put in a very smooth condition. In fact, for best results these surfaces should be polished. This reduction of frictional resistance is still further assisted by amply lubricating the surface of the sheet. A medium-grade cylinder oil is recommended for this purpose.

The pressure of the blank holder could be so great as to prevent all lateral movement of the sheet, in which case the forming would proceed only up to the ability of the metal to actually stretch in its unconfined area. The pressure of the blank holder, therefore, should be reduced to the minimum sufficient to keep the sheet flat. It will be clear from the foregoing that as the ultimate tensile strength of the metal increases, it can successfully overcome greater resistance against movement between the die and blank holder. As the thickness of the sheet increases, the blank-holder pressure necessary becomes less because the metal in itself, being thicker, will tend to resist buckling.

Furthermore, in planning the drawing of aluminum shells, it is generally considered impractical to have the diameter of the shell in the first draw less than 0.6 of the diameter of the original circle. If it is necessary to draw a shell exceeding these relationships, recourse must be had to doing so in two or more operations.

The high plasticity of aluminum results in a greater thickening of the metal as it converges toward the die than occurs with steel and brass and this demands a slightly greater clearance between the punch and the die than is common for other metals. In other respects, the forming of aluminum and its alloys employs the same general principles used for other metals, with the exception, especially with the pure grade, that intermediate annealing between draws is usually not required.

The sharpness of the radius over which the metal can be drawn and the amount of work that can be done will depend on the mechanical properties of the metal. Information regarding tensile strength, yield point and elongation offers a fair criterion of the workability of the metal. A material possessing a high elongation will stretch more than one with a low elongation, and a material wherein the ratio of yield point to tensile strength is low can be worked far more severely than one in which this ratio is high.

The same fundamental principles apply whether the work consists of drawing a shell or forming a right angle on a cornice-brake. In brake-forming operations, one must appreciate that as the ductility decreases the radius to which the metal can be successfully formed must be increased. Before any tools are planned, therefore, the minimum radius

over which the metal will bend should be ascertained. In all commercial metals there is a certain variation in properties from lot to lot; it would, therefore, be unsafe to assume that, because a certain sample of sheet $\frac{1}{8}$ in. thick successfully bent at 90° over a radius one-half its own thickness (namely, $\frac{1}{16}$ in.), all subsequent pieces of metal of this same grade and temper will do likewise. It is best to employ a radius somewhat larger than that determined by such tests.

Heat-treatable alloys have introduced some new practices. With other metals, when experience has shown a forming operation to be too severe, the procedure has been to ease up on the shape so as to work the metal less severely, do the work in two operations with an intermediate annealing instead of in one, employ metal of a softer temper, or adopt a combination of these. Another course is available in the case of the so-called strong aluminum alloys. This centers around the fact that the properties of these alloys can be altered by heat treatment.

Assume that one wishes to make a certain shape wherein the metal in the finished part should be in the fully heat-treated and aged condition, having a tensile strength of approximately 60,000 lb. per sq. in. Trial may indicate that this article cannot be directly formed from the heat-treated and aged metal. It may then be possible to take this metal, heat it to its heat-treating temperature, quench it, and perform the forming operation before aging has set in. The metal will harden spontaneously after forming and will acquire the fully heat-treated and aged condition.

Assuming that, even after quenching, the metal is still not sufficiently workable to form, the next possibility would be to use sheet in the annealed condition, form it, and then heat treat the formed article. Recourse to other means, namely, easing up on forming radius, should, of course, not be lost sight of. Very often the most satisfactory solution is a compromise among the several principles noted.

These ideas can be extended still further in the case of certain aluminum alloys which are hardened by artificial aging; for example, the previously mentioned special 17ST which develops tensile strength of just under 70,000 lb. per sq. in., with a yield point of 50,000 lb. per sq. in. This material behaves like duralumin in that it is quite workable immediately after quenching and hardens spontaneously at room temperature. This temper is given the designation of "special 17SW." One can follow the procedure outlined above for duralumin and then obtain still higher strength by artificially aging the formed article.

HOT FORMING

Aluminum alloys in the wrought condition are very malleable at elevated temperatures. Especially in recent months many structural

shapes, such as window and door posts in railway passenger cars, have been hot formed from heavy-gage sheet. The shapes in question could not have been formed cold.

In the hot forming of aluminum sheet, the principal factor to control is temperature. The most suitable temperature to employ will vary with the shape to be formed but in general it is advisable to employ the highest temperature at which the metal will not break. This is for the purpose of obtaining heat-treatment effects in the finished form. The quenching resulting from the contact of the relatively cold dies is sufficient to produce properties that are almost as high as can be obtained by giving the shapes a separate heat-treating operation. The desirable temperature, therefore, is about 950° F.

The tensile strength of the metal will decrease with increase in temperature and, in the case of shapes where the metal is under considerable tension during the forming operation, this tension may exceed the ultimate tensile strength of the metal at that temperature. In such cases it will be necessary to lower the forming temperature in order to build up the strength sufficiently. If the temperature necessary to give the required strength should be too low to give adequate heat treatment, it may be necessary to reheat the shape to a suitable heat-treating temperature, namely 950° F., and again insert it in the die for quenching and straightening. Wherever the shape requires more than one operation, it is desirable to perform all operations prior to the final one at relatively low temperatures, for example, 750° F., because at this lower temperature the metal can be handled more readily; its strength will be greater than at higher temperatures and the full heat-treatment effect must be obtained, after all, by the final heating.

The standard type of steel-forming equipment may be used; in fact, practically all of the hot forming of strong aluminum alloy sheet has, so far, been carried out in plants normally operating on steel. The one piece of equipment not usually found in such a plant is a furnace suitable for heating aluminum. Due to the lower temperatures for aluminum and the fact that the temperature of aluminum cannot be observed by color change, a furnace designed to control accurately at temperatures lower than those used for steel is necessary.

JOINTING

Aluminum may be joined by the usual methods of soldering, welding and riveting.

Soldering

Special solders are required for aluminum. There are many on the market, some of which are much better than others. The most satis-

factory of them, however, do not permit soldering with the same ease as is possible in the case of half and half with brass or copper.

The same general technique is employed as applies to half and half solder with brass, with the exception that the surfaces of the parts to be jointed must first be independently tinned and with few exceptions, this tinning requires a definite rubbing action. Aluminum solders will not wet aluminum as readily as half and half solder wets brass. Many aluminum solders require the use of a flux. The Aluminum Company of America has recently developed a solder which actually flows into crevices, such as a wire joint, with quite good results.

All aluminum solders so far developed are electro-negative to aluminum; hence, such a soldered joint, when exposed to wet conditions, will eventually disintegrate. There are, of course, many applications where this feature need give no concern. Soldering has been used for many years to plug holes in castings and to do general local repair work.

Welding

Welding of aluminum is done by autogenous and electric methods. Autogenous welding has been widely and successfully practiced for many years, especially with the pure metal and the less complex alloys. It is presumed that the reader is generally familiar with the apparatus and technique required for autogenous welding. Therefore, the following discussion will be confined to a few special phases.

Two types of flame are employed, oxyacetylene and oxyhydrogen. Choice of gas is determined by the following considerations. If the intensity of the flame is too great, the metal will be melted too rapidly for the operator to handle easily, with the result that a hole may be melted away at the joint. The repair of such a condition leaves a very unsightly joint. Furthermore, it is obviously difficult and sometimes impossible to bridge a large gap with molten metal. Therefore, as the temperature of the oxyhydrogen flame is considerably less than that of the oxyacetylene, and as the former, when properly adjusted, will melt ordinary-gage sheet as rapidly as the operator can work, the oxyhydrogen flame is recommended for light-gage small work. In the case of sheet $\frac{1}{8}$ in. or thicker, where considerable heat might be lost by conduction, the oxyacetylene flame may be the proper choice.

A further objection against the acetylene flame is the possibility of carbon being deposited by an improperly regulated flame. This carbon may interfere with the proper functioning of the flux and will retard coalescing of the molten metal.

All aluminum is covered with a thin film of oxide, which is so strong that even though two lumps of aluminum are melted and brought into

contact they will not unite unless this film is broken mechanically or removed in some other manner. In welding aluminum, difficulties due to this oxide film may be overcome by the "puddling" method, which consists merely in mechanically stirring the pool of molten metal, but this has the objection that the films of oxide, though broken up, still remain in the mass of metal. A flux is therefore almost universally used in the autogenous welding of aluminum. It is the duty of this flux to dissolve the oxide as welding progresses.

A good flux should have the following characteristics. It must have the ability to dissolve oxide very quickly and in such amounts as may be required. The melting point must be below that of the metal and it must not volatilize at the temperature to which it is subjected by the flame. The specific gravity of the molten flux with the oxide dissolved in it must be sufficiently less than that of molten aluminum so that it will quickly rise to the surface and thus carry the oxide out of the weld. Furthermore, the flux must not deteriorate in storage.

There are many aluminum fluxes on the market but not all of them meet the above requirements. Although good fluxes might be considered expensive, successful welding depends so considerably upon the quality of this flux that the choice of brand should not be decided by cost but solely by performance.

A common method of using flux is to dissolve it in water to the consistency of a thin cream and either apply it to the joint by means of a brush or dip the welding stick into the mixture. Sufficient flux will cling to the welding stick to supply the required amount as needed.

Aluminum welding fluxes, when permitted to remain on the metal and then subjected to moisture, will attack aluminum. It is, therefore, necessary to completely remove the flux and this should be done immediately after welding has been finished. For most work such as the manufacture of utensils, it is sufficient to wash the welded article in a tank of hot clean water. If the article is later to be painted, especially if the surface of the weld is dressed, such a simple wash may not be sufficient. In this case, the joint should be cleaned by live steam played against it; then it should be dipped in a hot 2 per cent. solution of nitric acid, followed by a rinse in clean hot water.

During welding, the torch should not be directed forward, as the flame might blow molten metal ahead of the actual welding where melting of the sides of the joint had not yet occurred, with the result that only a glueing action would result. Such a weld would obviously be weak.

The flame should be so applied that both sides of the joint will be heated and melted equally and simultaneously. With joints of unequal sections, it is thus necessary to direct the flame more against the heavier part. Greater speed is necessary in welding aluminum than in welding steel and in making a long seam the rate of progress gradually increases

as the whole part heats up. Once welding has commenced it should progress to completion without interruption. When making very long seams, it is desirable to tack the parts together at suitable spots. Though this will introduce short localized buckles, without such tacking the warping due to expansion and contraction will be cumulative and may result in cracking of the parts already welded or in such spreading or overlapping of the parts not yet welded that satisfactory results cannot be obtained.

Some difficulties arise in the welding of strong aluminum alloys due to their great tenderness just below the solidification temperature. Contraction stresses during solidification and cooling are quite severe and these may cause the metal to crack either in the weld itself or in the base metal immediately adjacent to the weld. This type of difficulty may be greatly minimized by using a welding stick of 5 per cent. silicon, 95 per cent. aluminum.

When considering whether a strong alloy joint should be made by welding, one must not lose sight of the fact that the metal in the weld is essentially a chill casting and consequently will have the properties of that particular alloy in its chill-cast state. Occasionally it may be possible to hammer the weld, thus putting the metal in the wrought condition, but this possibility is rather unusual. In the case of heat-treatable alloys, maximum heat-treatment effects cannot be obtained from the metal in the cast state. Therefore, one cannot expect to get the properties of the wrought, heat-treated metal in a welded joint by heat treating the assembly.

Another feature to bear in mind when welding heat-treated alloys is the effect of the heat of welding upon the adjacent metal. Careful explorations have shown that the metal immediately adjacent to the weld is usually heated to its heat-treating temperature and that the rate of cooling is sufficient to produce substantial heat-treating effects. A little farther away from the weld, the full heat-treating temperature has not been reached and at some location, about $\frac{1}{2}$ to $\frac{3}{4}$ in. in the case of sheet 0.064 in. thick, the temperature has only reached the annealing temperature for that alloy. As has been previously pointed out under the subject of annealing, it is necessary to hold a heat-treated piece of metal at elevated temperatures for a considerable time to produce maximum softness. Therefore, though this particular area of metal may be softened somewhat, it will not become completely annealed. The temper of the metal in such a joint consequently will vary considerably. Provided that the extra thickness in the weld has not been reduced by dressing and that the weld is clean and sound, the weakest part in such a joint will lie in an area on either side of the weld itself. A second heat treatment of the assembly will convert all the wrought metal into the heat-treated state.

Electric Welding

Electric-arc welding of aluminum is being investigated but to date it has not yet been made commercial. Percussion welding has also been tried out and has been used in the case of joining wire.

Spot welding has been developed to a stage where it is used in regular production, particularly with pure aluminum and some of the alloys. The equipment consists of a standard type of spot welder supplied with adjustments for varying the mechanical pressure, and current density. Some machines also permit automatic control of the time element, which is desirable, though not essential.

Due to the greater electrical conductivity of aluminum as compared to steel, higher current densities are necessary; consequently, for spot

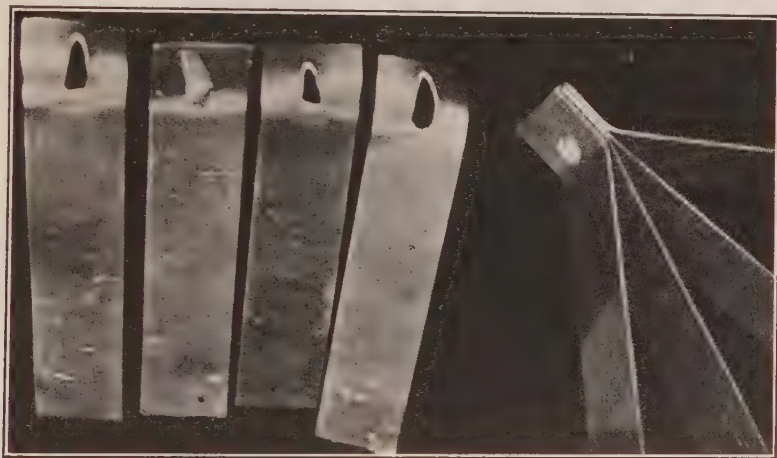


FIG. 2.—TEST OF SPOT WELD ON FOUR SHEETS OF 3S, EACH ABOUT 0.040 IN. THICK. NOTE THAT SPOT ITSELF HAS NOT BEEN PULLED APART. THE ABILITY TO TEAR THE SHEET INDICATES THE HIGH QUALITY OF THE JOINT.

welding aluminum, a machine of larger capacity must be employed than is required in the case of steel sheet of equal thickness.

The principal variables requiring control are mechanical pressure exerted by the electrodes upon the joint, current density, and the time of current passage.

The general scheme to follow in setting up the machine for a certain job is to reduce the mechanical pressure and current density to a point below that at which a spot will form and then increase the current density. If "spitting" or "spattering" is observed, it indicates insufficient mechanical pressure. The current density and mechanical pressure should be the lowest that will produce a good spot. A few trials will ascertain the most suitable setting. This should be judged by pulling apart sample welds. A satisfactory weld in pure aluminum is one in

which the spot will tear out of one sheet, rather than one in which the two pieces of sheet merely pull apart through the spot. The latter indicates incomplete fusion. Fig. 2 illustrates the failure of a good spot.

When using a machine with which the time is controlled by the movement of a foot pedal, the operator should occasionally make a joint with pieces of scrap sheet, to check the correctness of the time.

The shape of the electrode tip is important. The diameter at the contact surface should be between $\frac{1}{4}$ and $\frac{5}{16}$ in., the larger dimension for thicker sheet. The surface of the electrode should be slightly rounded. It has been claimed that a hemispherical surface will automatically reduce the current density as the electrode sinks into the metal and thus prevent excessive melting. In our experience, this expedient seems of dubious merit and carries the disadvantage of pro-

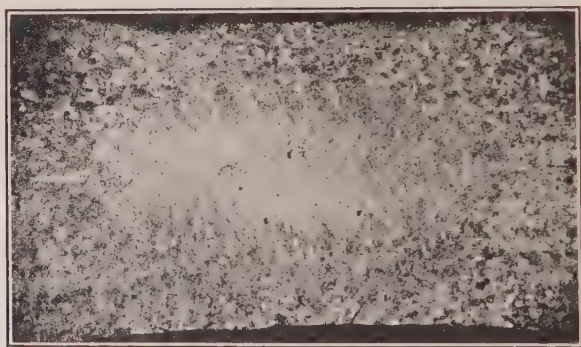


FIG. 3.—CROSS-SECTION OF A SPOT WELD. NOTE CONTACT SURFACES OF THE TWO SHEETS AT RIGHT AND LEFT. THE OVAL AREA IS THE SPOT.

ducing a deeper indentation than desirable. Occasionally it is necessary to have the minimum indentation on one surface. This can be accomplished by using a flat electrode on that side of the joint. However, the spots made in this manner will usually not be as uniformly good as when both electrodes are of equal size and slightly rounded.

In lining up the electrodes, it is important that the two contact surfaces be absolutely parallel at the instant of contact while making the joint.

Due to the greater current density required with aluminum, the electrodes should be water-cooled and this water-cooling should be extended into the tips themselves.

An important difference between the spot welding of aluminum and steel is the readiness of copper to alloy with aluminum. When plain copper electrodes are used, this alloying will commence to pit the surface of the electrode after about 20 to 40 spots, whereupon the electrode surface will have to be redressed. A recent development¹ consists in

¹ Patent applied for.

having chromium on the contact surfaces of the electrodes. A piece of chromium rod may be inserted in the copper tip or the tips may be plated with chromium. With such tips, it is regular production experience to obtain from 1500 to 2000 spots without redressing.



FIG. 4.—A SPOT-WELDED JOINT.

The range of thicknesses that can be handled varies with the capacity of the machine. A 20-kw. machine will spot weld two sheets of pure aluminum each 0.064 in. thick. Due to the lower conductivity of alloys,

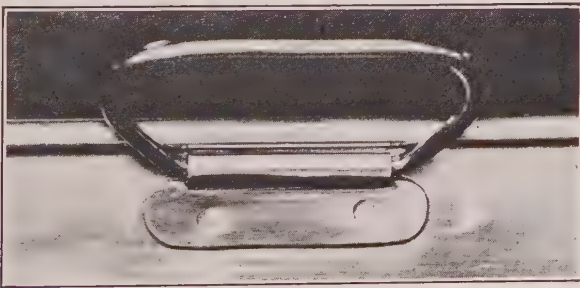


FIG. 5.—A SPOT-WELDED JOINT.

greater thicknesses of alloys can be spotted with this same machine. For example, in the case of 3S, this machine will handle sheet a little above 0.100 in. thick. Where two items of unequal thickness are to be joined, the total thickness of the joint may be somewhat greater but in that case

the maximum thickness of the thinner piece will be less. Three or four thicknesses may be spotted at one time.

The metal in the spot will be in the nature of a chill casting. However, when properly made, it is perfectly sound. Fig. 3 shows the cross-section of such a spot. Figs. 4 and 5 illustrate the general appearance of such a joint.

The strength of the joint, as in riveting, will depend on the number of spots. Table 7 gives a comparison between the strength of riveted and spotted pan handles.

TABLE 7.—*Comparative Strengths of Riveted and Spot-welded Handles*

Style of Fastening	Load Required to Break, Pounds	Remarks
Two rivets.....	354	Clip failed
Two rivets.....	510	Rivet sheared
Two rivets.....	534	One rivet sheared, one torn out
Two rivets.....	549	Both rivets torn out
Average.....	487	
Spot welded—two spots.....	420	Both spots torn out
Spot welded—two spots.....	383	Both spots torn out
Spot welded—two spots.....	445	Both spots torn out
Spot welded—two spots.....	503	Both spots torn out
Average.....	437	

More recently, experimental work has demonstrated the practicability of electric seam welding. This may be considered merely an extension of spot welding and the same technical conditions apply for both.

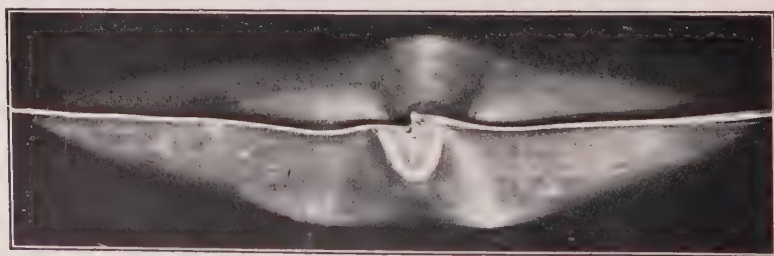


FIG. 6.—TWO PIECES OF METAL SEAM WELDED AT EDGES, WHICH HAVE BEEN SUBJECTED TO HYDROSTATIC PRESSURE.

Fig. 6 illustrates the character of such a joint. This part was made by taking two pieces of flat sheet, welding around the border, and then applying hydrostatic pressure to the parts through a plug previously fastened to one of the sheets. Had the welding taken place only in

spots, it would not have been possible to generate sufficient pressure between the sheets to force them apart into the pillowlike shape noted.

Riveting

The properties of the metal both in the material to be joined and in the rivet must be considered. When riveting soft aluminum, the metal will tend to spread, leaving a wavy edge. This action is due to the greater plasticity of aluminum and can be avoided by placing the rivets farther from the edge of the sheet than is standard with steel. For the same general reason, rivet holes may get out of coincidence if riveting is performed progressively from one end. To avoid this, the work should be held together by temporary bolts scattered along the joint or by riveting at random.

Strong aluminum alloys require special consideration. Due to the low plasticity of these alloys in the heat-treated state, thin heads, such as the brazier type, should be avoided. The height of the head along a line corresponding with the circumference of the shank should not be less than one-half of the shank diameter. Such a relationship is necessary to avoid overworking and damaging the metal in the head.

Should the rivet head be formed by a great many light blows, the surface metal will receive a peening action and consequently this surface metal may become severely overworked before the head has been formed. The ideal action would be to form the head by one continuous squeezing movement, therefore a compression type of riveter is to be preferred. When a hammer must be employed, it should be larger than would normally be selected for steel rivets of equal dimension.

When upsetting of heat-treated and aged rivets cannot be accomplished without serious damage to the metal, as indicated by a tendency for the rivet head to pop off when subjected to stress or by slight cracking of the rivet head, recourse should be had to heat treating the rivets and heading them shortly after they have been quenched. They will then age spontaneously and acquire the heat-treated state in the assembly. The operation of heating and quenching need not cause concern, as it can be done in a very small inexpensive nitrate pot and the rivets may be used within one hour after quenching.

In large construction work, at times, it may be desirable to employ hot driven steel rivets in the assembling of strong alloy shapes. This raises the question whether the heat-treated material will be softened by the heat from the rivet. Investigation has shown that the diameter of the hot steel rivet may be as great as eight times the thickness of the joint before any softening effects can be noted in the aluminum immediately adjacent to the rivet shank. Such proportions are seldom, if ever, reached in practice and therefore one may assume that no trouble will be encountered.

DISCUSSION

E. LUNN, Chicago, Ill.—What thickness of aluminum is considered possible to spot weld successfully? The Illinois Central suburban cars used in electric service have a good deal of aluminum on them, and the aluminum doors were spot welded. So far as I know there has not been a single spot weld that has loosened. In some experience with sheets up to $\frac{1}{8}$ in. thick, the welds were perfect.

I have in my possession a sample of welding. The metal is $\frac{1}{8}$ in. thick. The area of the spot is nearly $\frac{1}{2}$ in. In tearing the two pieces apart under shear the break came at 1200 lb. It seems possible to go to even thicker aluminum than that with good results.

P. V. FARAGHER, New Kensington, Pa.—I should say that the thickness of material depends to some extent on the composition of the metal. The alloys naturally have a higher resistance than the pure metal and it is possible to go to heavier thicknesses with those alloys than with the pure metal.

The machine which we have in our plant enables us to go up to 0.064 in. with pure metal and to rather heavier gages than that with the manganese-aluminum alloy—the 3S alloy, as we designate it. Also, one of the sheets may be heavier than that, while the other is thinner. I do not believe we are in a position to say just what are the limits on our machine, but we do commercially carry out the operation on the particular sizes I have mentioned.

Mr. Nagel has indicated in his paper the 0.064 thickness of aluminum. With the 3S alloy 0.100 in. can be handled, as he says, but we would not say that those are the ultimate possibilities. Those are the things which we have done and which we can safely tell to prospective users.

A. D. CAMP, Buffalo, N. Y.—At the Buffalo Fabricating Division of the U. S. Aluminum Co. considerable experimental and production work has been done with the spot welding of aluminum sheet. We have successfully welded 51SW sheet as thick as $\frac{3}{16}$ in. for each sheet, and commercially pure aluminum (2S metal) of the same thickness can also be readily welded.

Tensile-strength tests of spot-welded aluminum and its alloys indicate that the strength of sound welds is, roughly, directly proportional to the area of the spot. For that reason, unless other considerations limit the size of the spot, we use fairly large welding tips. We have found that tips $\frac{5}{16}$ in. in diameter give very satisfactory spots when the conditions of the machine (current density, time of application) and pressure have been properly worked out.

As a preliminary to spot welding, it is very desirable that the machine be properly lined up, so that the contact surfaces of the electrodes are exactly parallel and carefully centered. With eccentric contacts the current is localized over a constricted area, thereby causing blowholes and unsound spots. In production welding it has been found safest to use slightly crowned electrode tips, which can be most easily adjusted by ordinary operators.

Though spot welding of aluminum is now being extensively employed in many shops, the process is still in a state of rather intensive development, which will probably result in many improvements over our present practice.

Machining Aluminum

BY R. L. TEMPLIN,* NEW KENSINGTON, PA.

(Detroit Meeting, September, 1927)

THE increasing use of aluminum and its alloys in commercial fields has demanded a better understanding of their machining properties. This fact is exemplified by problems that have arisen in the automotive and airplane industries, but many in other fields might be cited. As pure aluminum and its alloys in their various commercial conditions show appreciable differences in their machining properties, it is not surprising that quite divergent solutions have been offered for the machining problems encountered. However, if the fundamental requirements of the most suitable cutting tools for these metals are understood, these machining problems lend themselves more readily to satisfactory solutions.

Since the machining of free cutting brass and mild steel is understood by most persons accustomed to working these metals, it may serve our purpose better to first make a general comparison of the tools more commonly used in machining these metals with the tools most suitable for machining aluminum, then proceed to a more specific discussion of the individual tools.

COMPARISON OF CUTTING TOOLS

Cutting tools commonly used for machining free cutting brass usually have little, if any, top and side rake; they are ground on a medium to coarse abrasive wheel and used without any cutting compound or with a cutting compound that has a paraffin base. Those ordinarily used for steel have some top and side rake, are usually ground on a medium to fine abrasive wheel, and are often used with soluble-oil cutting compounds. The proper tools for aluminum and its alloys should have appreciably more side and top rake than the tools for cutting steel; should have very keen edges obtained by grinding with fine or very fine abrasive wheels supplemented in many cases by hand stoning with an oil-stone; and should be used with suitable cutting compounds whenever possible. In many cases, tools suitable for machining aluminum and its alloys are not appreciably different from tools commonly used for cutting hardwoods.

The front clearance of a tool most suitable for machining aluminum and its alloys should be about 6° , the top rake from 30° to 50° , making the total angle of the cutting edge of the tool from 35° to 55° . A side

* Chief Engineer of Tests, Aluminum Co. of America.

rake of from 10° to 20° will materially assist in the cutting action of the tool. The specific values that should be used for these different angles must in many cases be governed by the work being done and the requirements of the machine in which the tool is used. The values given here usually will produce the best results, but in some cases departures may be made from them, depending on the particular alloy being machined, the type of tool and the conditions under which it is used.

In all cases it is quite essential that the cutting edges of the tools shall be keen, smooth and free from grinding-wheel scratches, burrs or wire edges. This requirement can hardly be overemphasized, as upon it depends, to a large extent, the success of machining aluminum and its alloys. Keen tool edges are best obtained by finish grinding on a fine or very fine abrasive wheel followed by hand stoning with a fine or very fine oil-stone, taking care to see that neither the angles nor the contours of the cutting edge are appreciably modified during the stoning operation.

An attempt has been made to show the character of the machined surfaces that will result from using different kinds of planer tools on wrought commercially pure aluminum. In the first instance (see Fig. 1), the material was machined with a tool frequently used for machining free cutting brass. The tool had a total included cutting angle of about 82° with no top or side rake. Fig. 2 shows the machined surface obtained with a tool such as is often used in machining mild steel. This tool had a top rake of 14° and a side rake of 16° . Fig. 3 shows the same material machined with a tool ground in accordance with the recommendations given for machining aluminum. This tool had a top rake of 50° , a side rake of 20° and a total angle of cutting edge of 35° .

In each of these cases the material was machined in a shaper using a feed of 0.022 in. per cut and a speed of 77 strokes per minute. The depth of cut was about $\frac{1}{64}$ in. By way of comparison, some of the same material was cut in a microtome (see Fig. 4), using a blade having a total included cutting angle of 44° . The photographs of the machined surfaces were taken under direct illumination using a magnification of 10 X. The first view in each case shows the surface obtained when using soluble cutting oil as a lubricant and the second view when using a mixture of equal parts of lard oil and kerosene.

When a blunt-edged tool, suitable for brass, is used for machining aluminum, the chip is not sheared from the piece being machined but is pulled off from the work just ahead of the cutting edge of the tool, leaving a rough surface on the work. With the continued use of such a tool, small particles of aluminum adhere to the cutting edge of the tool, soon build up and form a projection of hard worked aluminum, which tends to function as the cutting edge of the tool. However, this projection of hardened aluminum, while appreciably harder than the material being machined, is not of sufficient hardness to cut the aluminum stock

1

2

3

4

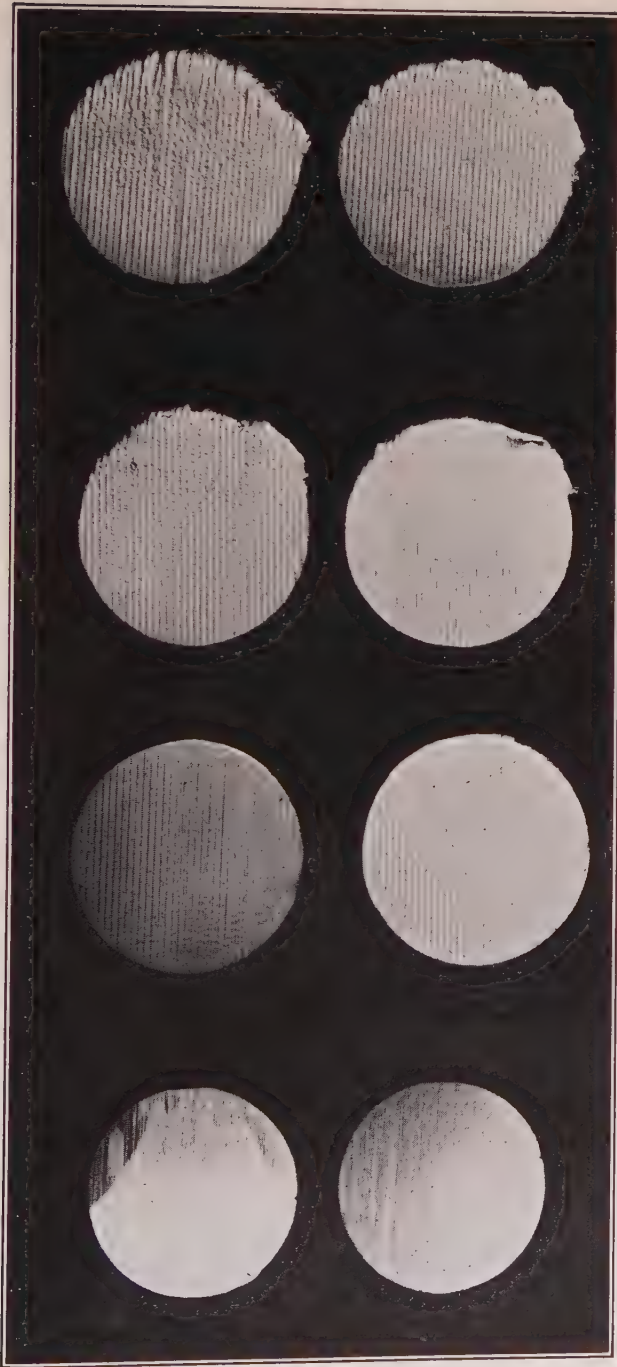


FIG. 1.—ALUMINUM MACHINED WITH A PLANER TOOL SUCH AS IS USED FOR MACHINING FREE CUTTING BRASS.

FIG. 2.—ALUMINUM MACHINED WITH A PLANER TOOL USED FOR MACHINING STEEL.

FIG. 3.—ALUMINUM MACHINED WITH A TOOL PROPERLY GROUND FOR MACHINING ALUMINUM.

FIG. 4.—ALUMINUM MACHINED WITH A MICROTOME.

properly; instead, it causes excessive heating of both the tool and the work, through friction with the stock and the resultant chip. Decreasing the cutting-edge angle of the tool lessens the extent to which the aluminum is deposited on the tool, until a point is reached where little, if any, metal will stick to the cutting edge; that is, when the angle of the cutting edge is small enough, the tool will cut the chips from the work and not tear or pry them off. In order to obtain a smooth surface on the work, the cutting tool should curl the chips as little as possible.

LATHE TOOLS

Outside turning tools for use in a lathe when machining aluminum and its alloys may be of the form suggested in Fig. 5, but tools of this kind, when prepared from the usual tool-bit stock, require considerable grinding in order to produce the desired shape and it is sometimes difficult to main-

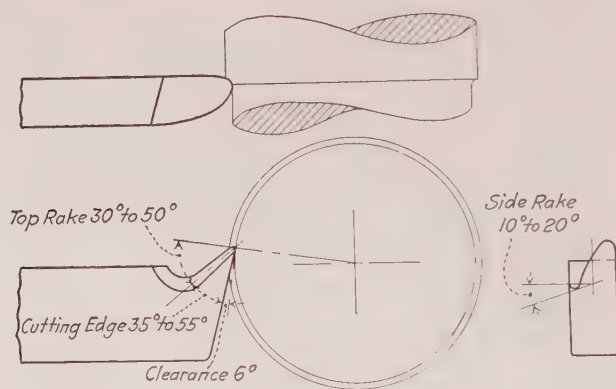


FIG. 5.—LATHE TOOL THAT MAY BE USED WITH ALUMINUM.

tain the values for the different angles when regrinding. A much better tool is shown in Fig. 6. The bit of this tool is made from annealed high carbon or high-speed steel-rod stock, then properly hardened and tempered. Resharpening is readily accomplished by holding the bit by its shank in the chuck or collet of a tool-grinding machine or an engine lathe, then simply grinding off the outside diameter until a keen edge is obtained on the bit. After each grinding, the tool should be stoned as indicated previously. Using such a tool and resharpening procedure, it is comparatively easy to maintain the desired shape throughout the tool's useful life. Also, this tool has proved more economical than those ground from square or rectangular tool-bit stock, and possesses certain adjustable features. When the clamp screw of the tool-bit holder is loosened, the bit may be rotated to various positions and thus be adjusted to different working conditions. Tools of this form may be used for both

rough turning and finishing cuts but where the same tool is used for both it should be rested before being used as a finishing tool. With some modifications, either of these two forms of tool may be adapted for boring operations.

These tools, like most others suitable for machining aluminum and its alloys, tend to produce continuous chips, which usually are curled only a little when the tools are functioning properly. Decreasing the top and side-rake angles tends to curl the chips more and hence to break them up. The extent to which this may be done and yet obtain the desired surface finish depends largely on the particular alloy that is being machined.

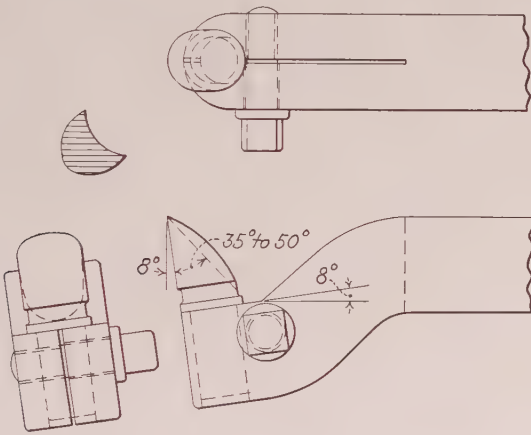


FIG. 6.—LATHE TOOL RECOMMENDED FOR USE WITH ALUMINUM.

Pure aluminum and many of its alloys are capable of being machined to a mirrorlike surface, but this surface is easily scratched by the chips when they come in forcible contact with it. The chips receive an appreciable amount of working during their making and are much harder than the stock from which they are cut.

Parting tools for machining aluminum and its alloys should have from 12° to 20° top rake and be stoned so that their cutting edges are keen and smooth. With such tools the front clearance angle should be decreased to about 3° or 4° .

Facing tools should be ground so as to have a side rake similar in amount to that indicated for the top rake of the outside turning tools.

Circular forming tools as used in automatic screw machines are sometimes difficult to design so that they will machine aluminum and its alloys properly. In such cases best results are often obtained by using a roughing tool first and following by a very light finishing cut with the forming tool.

PLANER AND SHAPER TOOLS

The tool shown in Fig. 6 can be readily adapted to planer and shaper work by using a holder, as shown in Fig. 7. Here again the tool may be used for both roughing and finishing work when machining aluminum,

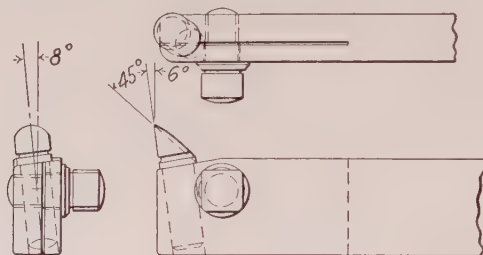


FIG. 7.—PLANER AND SHAPER TOOL FOR MACHINING ALUMINUM.

but a side cutting tool, as shown in Fig. 8, can be used to better advantage for still heavier roughing cuts.

When finishing aluminum in a planer or shaper, care must be used to prevent the tool striking or rubbing on the finished surface during the

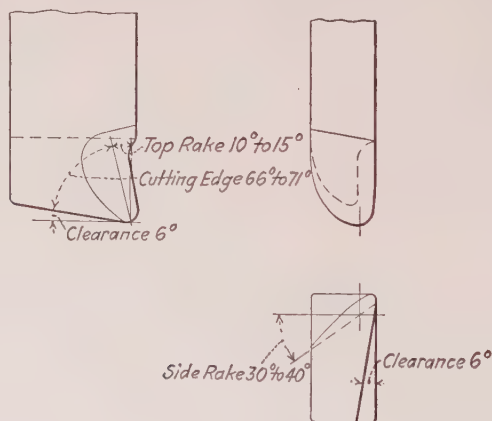


FIG. 8.—PLANER TOOL FOR ROUGHING ALUMINUM.

return stroke of the tool. If the tool strikes, the work may be scratched and the thin edge of the tool broken.

MILLING CUTTERS

Milling cutters, straddle mills, end mills and similar cutters work to best advantage in machining aluminum and its alloys if they are of the coarse-tooth spiral type and have a considerable amount of top rake on their cutting edges. Similar tools have been found to work very well when machining steel. In some instances milling cutters with nicked

teeth assist in decreasing the chip size. Face-milling cutters with inserted teeth can be made that will work very well when machining aluminum. Such cutters should be designed so that the inserted teeth have appreciable top and side rake, as previously indicated. The comparatively new helical milling cutters, primarily designed for machining steel, work especially well with aluminum and its alloys if the cutting edges are provided with suitable top rake. The same may be said of staggered-tooth milling cutters.

THREADING TOOLS

Excellent threads may be chased in even the softest aluminum in an engine lathe using a single pointed threading tool with considerable top and side rake. The tool must be ground so as to give the required thread contour. Hand and machine taps will produce smooth and accurate threads in aluminum if they are of the spiral flute-ground thread type. Experience has shown that such taps should have a right-hand spiral flute when intended to cut a right-hand thread and the spiral angle should be similar to that used in an ordinary twist-drill. Very satisfactory taps for use in aluminum have been made by chasing threads on annealed high-carbon twist-drills followed by retempering and finishing. Taps which have a short spiral ground on their front end, such as the "Gun" tap, will often work satisfactorily in aluminum when there is room for the chips to be forced ahead of the tap and when the thread to be cut is not tapered, but taps of this type are not satisfactory for taper threads or for use as bottom taps. When using spiral fluted taps, especially in automatic screw machines, it has been found advantageous to grind a top rake on the back of the lands so that there will be less tendency for the tap to seize when backing out of the work.

Slightly oversize taps often assist materially in maintaining the required dimensions of holes in aluminum and its alloys. That is, aluminum, on account of its lower modulus of elasticity, has more recoverance after a tapping operation than steel and this is best compensated for by the use of slightly oversize taps.

Thread chasers for self-opening die heads and collapsible taps should be ground with appreciable top and side rake. Certain makes of these tools lend themselves more readily than others to modifications of their cutting angles.

TWIST-DRILLS

Ordinary twist-drills sometimes give trouble when machining aluminum and its alloys. Like all other cutting tools for aluminum, twist-drills should have keen edges, and a copious amount of cutting compound should be used with them. In some instances the single fluted twist-drills used in drilling hardwood have been found superior to the usual form

of drill. A still better drill for aluminum is one in which the flutes have a greater spiral angle; that is, more twists per inch. Examples of these drills together with a standard twist-drill are shown in Fig. 9. Straight



FIG. 9.—THREE TYPES OF TWIST-DRILLS, $\frac{3}{8}$ IN. DIA.

- a*, Single flute twist-drill, 40° spiral angle.
- b*, Double flute or standard twist-drill, 24° spiral angle.
- c*, Special double fluted twist-drill, 47° spiral angle.

fluted twist-drills such as are often used in drilling brass are quite unsuited for drilling aluminum and its alloys.

REAMERS

Reamers of the spiral fluted type produce by far the best results when machining aluminum and its alloys. Reamers of this type have come into quite general use for machining steel and therefore need not be further discussed.

SAWS

Saws most suitable for cutting aluminum should preferably be of the coarse-tooth type and have some top rake on the teeth. In many cases, saws which are used for cutting hardwood will be found quite satisfactory for sawing aluminum if they are used with a lubricant. Hand hack-saw blades of the "wavy-set" type work especially well with aluminum.

FILES

Ordinary files, especially those with fine teeth, do not work well on aluminum because the cuttings stick in the teeth, but there are a number of coarse-tooth files, such as the "Vixen," "Shearkleen" and "Premier," which work very well for filing aluminum and its alloys. The success of these files depends to a large extent upon the top and side rake of their cutting teeth. Quite recently chromium-plated files have appeared on the market, and give much promise of being eminently satisfactory for use on aluminum irrespective of the size and form of teeth.

GRINDING WHEELS

Most manufacturers of grinding wheels and abrasives have had so much experience in furnishing abrasive tools for cutting aluminum that they are able to make quite definite recommendations regarding type of wheel, grain size, bond and wheel speeds for the various grinding problems submitted.

CUTTING SPEEDS AND FEEDS

Quite wide ranges for cutting speeds and feeds have been used in machining aluminum and its alloys. Generally, aluminum can be machined to best advantage by using comparatively high speeds and fine to medium feeds. Surface speeds varying from 500 to 800 ft. per min. are possible under some conditions with ordinary carbon-steel tools, and appreciably higher speeds may be obtained with high-speed steel tools. The feed may vary from as much as $\frac{1}{4}$ in. for roughing cuts to a few thousandths of an inch for finishing cuts. The particular values to be used for speed and feed are usually dependent on the character of work being done, the type of tool used, the lubricant used and the machine tool with which the work is done.

Cutting speeds faster than those ordinarily used for free cutting brass have been used with success in some instances, while in others better results have been obtained by using slower cutting speeds. Usually, the finer the feed, the higher the speed; and the more curl there is to the chip, the slower the speed. Slower speeds and heavier feeds give better results when a heavier cutting compound is used. An increase in the amount of metal removed from the stock in a given time may often be obtained to better advantage by increasing the speed rather than the feed when using the tools described, but tools having keen, thin edges will not work satisfactorily when chattering occurs, as this action will break off the edge of the tools.

Aluminum, like other metals, tends to show a rise in temperature when machined with coarse feeds, and since the linear coefficient of expansion of aluminum is appreciably higher than steel, for example, the

finished work may fail to meet the required dimensions unless due allowance is made for the expansion of the metal. In engine lathe work, a common trouble when using heavy coarse-feed cuts is the excessive friction set up on the lathe centers due to expansion of the metal with rise in temperature. When appreciable heating of the work does occur it should be cooled before calipering and finishing to size, in order that the required dimensions may be obtained.

CUTTING LUBRICANTS OR TOOL COOLANTS

Some of the alloys of aluminum have been machined successfully without any lubricant or cutting compound, using tools of the form described, but in order to get the best results, some form of lubricant is quite desirable. For many purposes a soluble cutting oil is good. Ordinary carbon oil or kerosene will often serve but usually it works better when mixed with pure lard oil. The proportions of kerosene and lard oil should be governed by the character of the work being done and the cutting speed and feed being used. An all-round mixture for general use will be obtained by using equal parts of kerosene and lard oil. Some machinists prefer to add a little turpentine to this mixture, but the advantages obtained are doubtful. For heavy cuts and slow feeds such as in roughing work or tapping, pure lard oil has been found to give very satisfactory results.

Cutting compounds having a paraffin base, such as are used in machining brass, are quite unsatisfactory for machining aluminum. For milling, sawing and drilling, the soluble cutting oils are satisfactory and more economical than the kerosene or kerosene and lard oil lubricants.

When the work has been rough machined without using a lubricant, sometimes small particles of the metal adhere to the cutting edge of the tool. These should be removed by stoning the tool before using it for finishing work. A continuous and copious supply of lubricant should be fed to the tool, in order to produce the best results.

COMPARATIVE MACHINEABILITY OF DIFFERENT ALUMINUM ALLOYS

In order to give some idea of the differences in the machineability of some of the more common aluminum alloys in both the wrought and cast conditions, the specimens shown in Fig. 10 were prepared. All of these were machined on a shaper using the same tool, speed, feed and a mixture of equal parts of lard oil and kerosene as a cutting compound. The comparative roughness or smoothness of the surface finish obtained under such circumstances may be used as an index of the relative machineability of the different metals. The aluminum-silicon alloys No. 43 and No. 47 are perhaps the most difficult to machine, while those of the duralumin type, 17S-T and No. 196 heat treated have the best machining properties.

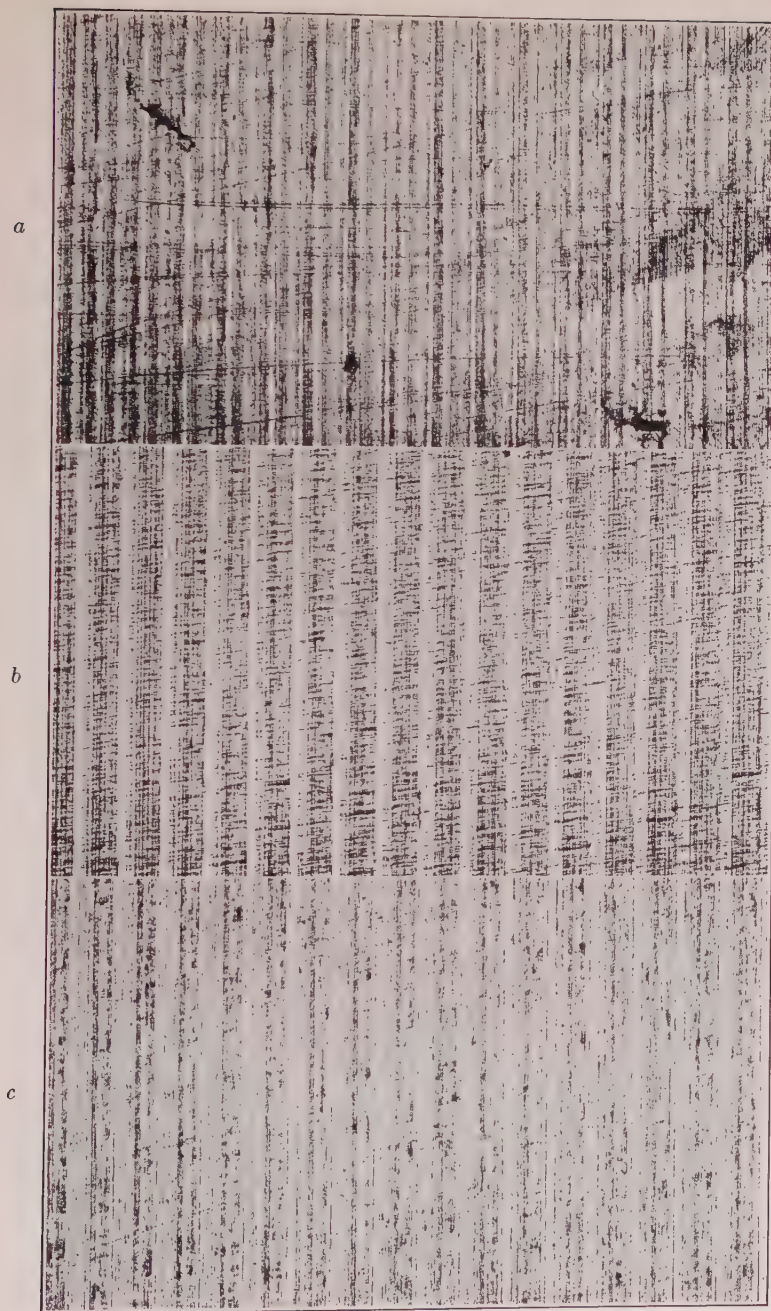


FIG. 10.—SURFACE FINISHES OF ALUMINUM ALLOYS MACHINED UNDER THE SAME CONDITIONS. $\times 10$.

- a, No. 7A. Very pure wrought aluminum.
- b, 17S-T. Heat-treated wrought duralumin.
- c, 3SO. Annealed wrought aluminum-manganese alloy.

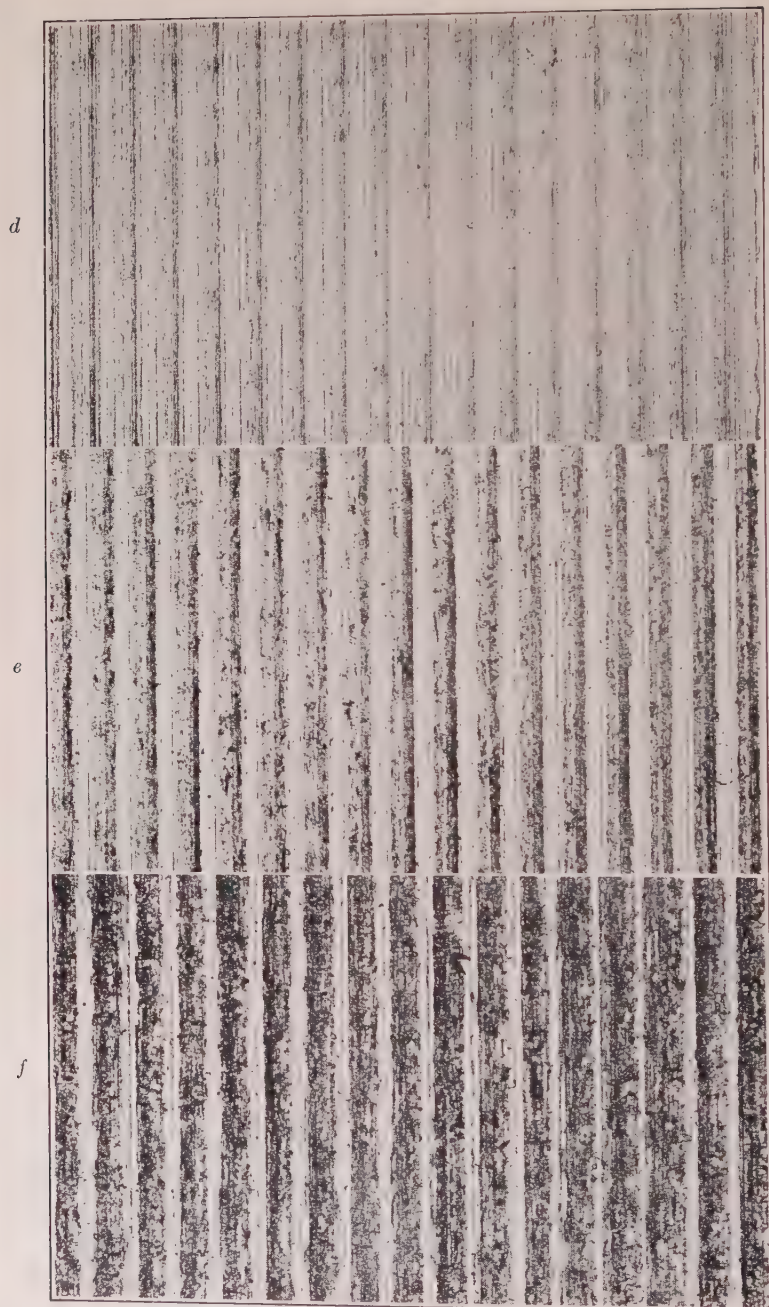


FIG. 10.—SURFACE FINISHES OF ALUMINUM ALLOYS MACHINED UNDER THE SAME CONDITIONS.—(Continued).

d, 3SH. Hard wrought aluminum-manganese alloy.

e, 25S-O. Annealed aluminum alloy of the duralumin type.

f, 25S-W. As-quenched aluminum alloy of duralumin type.

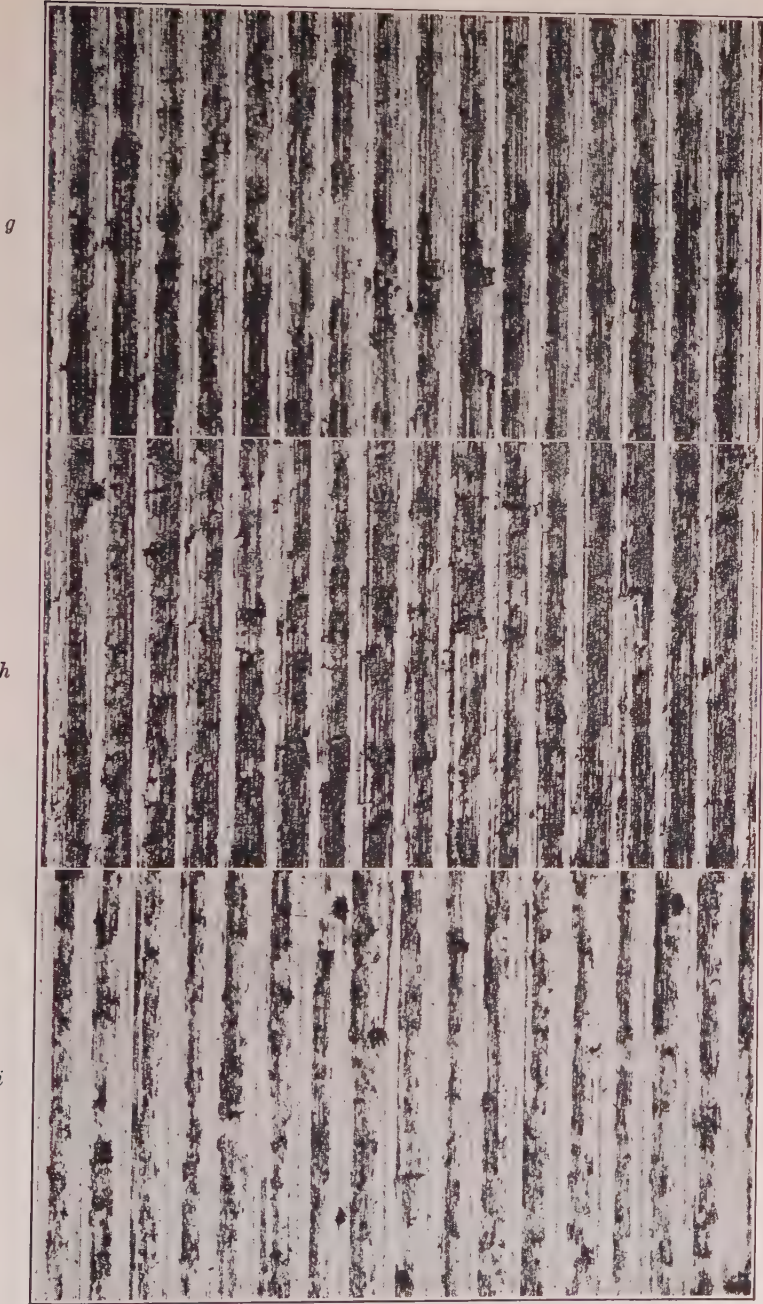


FIG. 10.—SURFACE FINISHES OF ALUMINUM ALLOYS MACHINED UNDER THE SAME CONDITIONS.—(Continued).

g, No. 106. Cast aluminum-manganese alloy.

h, No. 195-HT. Heat-treated cast aluminum alloy of duralumin type.

i, No. 142. Cast aluminum-nickel-copper-magnesium alloy (Y alloy) not heat treated.

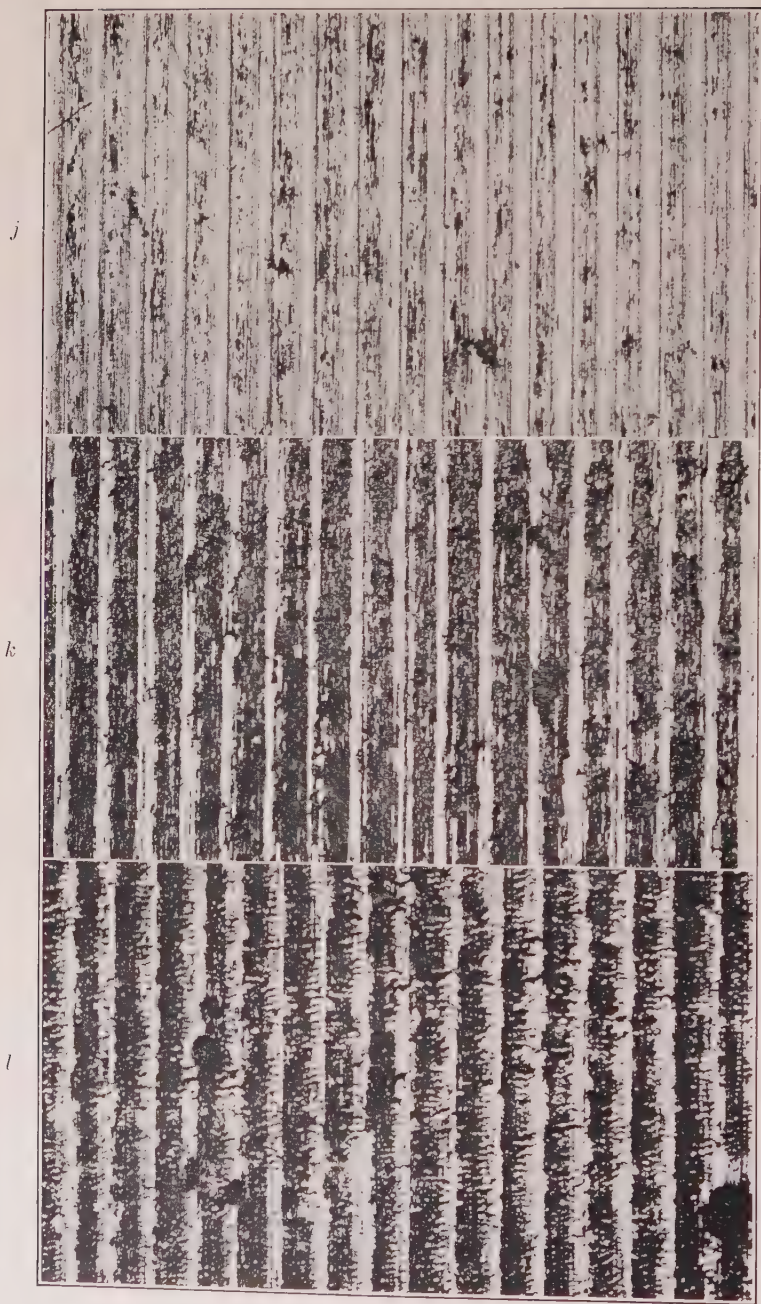


FIG. 10.—SURFACE FINISHES OF ALUMINUM ALLOYS MACHINED UNDER THE SAME CONDITIONS.—(Continued).

- j*, No. 112. Cast aluminum-copper alloy.
- k*, No. 43. Cast 5 per cent. silicon-aluminum alloy.
- l*, No. 47. Cast and modified 13 per cent. silicon-aluminum alloy.

In conclusion, the fact should again be emphasized that the best tools for machining aluminum and its alloys have keen, smooth edges, with appreciably more than the customary amount of top and side rake.

ACKNOWLEDGMENT

Acknowledgment is made of the assistance of E. H. Dix, Jr., metallurgist of the Aluminum Co. of America, under whose supervision the photomicrographs were prepared.

DISCUSSION

R. L. TEMPLIN.—More recently a few rather brief articles have appeared, especially in foreign literature, on the subject of machining aluminum, but there has not been an opportunity to prepare a complete bibliography on the subject.

The work which this paper covers was not done hurriedly but extended over some eight or nine years' experience in machining. About seven or eight years ago, some of the material presented in the present paper was issued in the form of a pamphlet by the sales department of the Aluminum Co. of America. At the time of the issuance of that pamphlet very little was available in the literature on the subject, and we were requested to bring that information up to date and present it at this time. We are indebted to Mr. Dix for the slides.

Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity

BY E. H. DIX, JR.,* AND A. C. HEATH, JR.,† NEW KENSINGTON, PA.

(Detroit Meeting, September, 1927)

THE importance of aluminum-silicon alloys in the light alloy field is now generally recognized. Where silicon was once considered detrimental to the properties of aluminum, useful alloys now contain as much as 13 per cent. Furthermore, silicon is present as an impurity in aluminum of even the purest grades.

Iron is another important impurity in aluminum and like silicon is found in small quantities in the purest aluminum available today. The manner of occurrence of iron and silicon in commercially pure aluminum and many of its alloys exerts a very pronounced influence upon their properties. The effect of large quantities of iron in aluminum-silicon alloys is so detrimental that it has been found necessary to limit the allowable maximum percentage to as low a figure as is consistent with quantity production and satisfactory physical properties. The intimate relation existing between iron and silicon in aluminum and aluminum alloys makes necessary a more complete knowledge of this ternary system.

This paper is divided into two principal parts, dealing respectively with aluminum-silicon solubility equilibria and the constitution of aluminum-iron-silicon alloys.

PART I.—ALUMINUM-SILICON ALLOYS

The early work on this system was largely confined to determining the general form of the diagram and in this respect the results are in good agreement. Briefly, aluminum and silicon form a simple eutectiferous series without compounds. Until recently the solid solubility of silicon in aluminum had not been accurately determined. Fraenkel¹ (1908) stated that aluminum will retain 0.5 per cent. silicon in solid solution. Rosenhain, Archbutt and Hanson² gave the maximum solubility as about 1.50 per cent. and added that "this solubility does not appear

* Metallurgist, Research Bureau, Aluminum Co. of America.

† Assistant metallurgist, Research Bureau, Aluminum Co. of America.

¹ W. Fraenkel: Über Silicium-Aluminium legierungen. *Ztschr. für anorg. Chem.* (1908) **58**, 154.

² W. Rosenhain, S. L. Archbutt and D. Hanson: Eleventh Report to Alloys Research Committee of Institution of Mechanical Engineers. (1921) 212.

to decrease appreciably as the temperature is lowered." Otani³ determined the solubility of silicon in aluminum by electrical resistivity measurements at three different temperatures, the lowest of which was 360° C. and attempted to check the results at two of the temperatures by a chemical analysis method of doubtful reliability. At about the same time Gwyer and Phillips,⁴ using the usual metallographic methods, determined the solubility from the eutectic temperature to 500° C.

Köster and Müller,⁵ using annealing periods of only 6 hr. and the same doubtful chemical method as Otani, have also published a solubility curve. The lowest temperature at which they determined the solubility was 300° C. Bosshard⁶ in a paper primarily devoted to a determination of the effect of relatively small amounts of additional elements on the electrical conductivity of aluminum, obtained an indication of the solubility at two different temperatures. His aluminum contained 0.2 per cent. iron. The numerical results obtained by these investigators will be found, compared with those obtained in the present investigation, on page 178. The eutectic temperature and composition seem to have been satisfactorily established by Edwards⁷ and Gwyer and Phillips.⁸

The present investigation was undertaken in accordance with the plan of the Aluminum Co. of America of investigating the constitution of aluminum alloys, using aluminum free from appreciable amounts of impurities. At the time work was started (in the latter part of 1925) no accurate data on the solid solubility of silicon in aluminum had been published, and although several investigators have subsequently published their results, it was felt that the publication of the writers' findings would be desirable, particularly as this work has covered the solubility at a temperature as low as 200° C. Other investigators have not concerned themselves with the solubility at this low temperature, probably because of the long time required to produce equilibrium. Hence the results obtained in this investigation, which incidentally showed a much lower solubility than would be expected from the curves of other investigators, have been of considerable interest. The maximum annealing time used in determining the solubility at 200° C. was 3100 hours.

³ B. Otani: Silumin and Its Structure. *Jnl. Inst. Metals* (1926) **36**, No. 2, 243-267.

⁴ A. G. C. Gwyer and H. W. L. Phillips: Constitution and Structure of Commercial Aluminum-Silicon Alloys. *Jnl. Inst. Metals* (1926) **36**, No. 2, 283.

⁵ W. Köster and F. Müller: Über die Löslichkeit des Siliziums im Aluminium. *Ztschr. für Metallkunde* (1927) **19**, No. 2, 52.

⁶ M. Bosshard: The Electrical Conductivity of Pure Aluminum. Aluminium-Industrie-Aktiengesellschaft, Neuhausen. Schweiz. Elektrotech. Verein *Bull.* (March, 1927) **18**, 113-122.

⁷ J. D. Edwards: Thermal Properties of Aluminum-Silicon Alloys. *Chem. & Met. Eng.* (1923) **28**, 165.

⁸ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

The object of this work was to determine the solid solubility of silicon in aluminum, establish the position of the solidus at the aluminum end, and to check the eutectic temperature and concentration.

PREPARATION OF ALLOYS

Electrolytically refined aluminum of high purity was used; analysis showed the following composition:

M No.	ALUMINUM, PERCENT- AGE BY DIFFERENCE	COPPER, PER CENT.	IRON, PER CENT.	SILICON, PER CENT.	MANGA- NESE, PER CENT.	TITAN- IUM, PER CENT.	VANAD- IUM, PER CENT.
1932	99.951	0.021	0.012	0.013	Nil	0.002	0.001

The silicon used had the following composition as shown by analysis:

M No.	SILICON, PER- CENTAGE BY DIFFERENCE	COPPER, PER CENT.	IRON, PER CENT.	MANGANESE, PER CENT.	ALUMINUM, PER CENT.	TITANIUM, PER CENT.
537	98.64	Nil	0.66	0.04	0.56	0.10

The appreciable iron content of the silicon was responsible for the higher percentages of iron in high-silicon alloys. However, the alloys for the solubility work contained a maximum of 0.05 per cent. iron.

All alloys (Table 1) were prepared either by melting together aluminum and a 20 per cent. aluminum-silicon hardener, or by first melting pure aluminum and then adding silicon as the pure element. The melting was done in a small Hoskins electric crucible furnace, using Acheson graphite crucibles holding 700 g. of aluminum. The melt was stirred and skimmed just before pouring the sample for analysis, which was cast in the shape of a thin plate, and then the remainder of the melt was poured into an open horizontal mold, giving a bar of cross-section $\frac{1}{2}$ by $\frac{5}{8}$ in. and 9 in. long. This mold has been described in a previous paper⁹ from these laboratories.

COOLING CURVES

In addition to the cooling curves which were taken on several alloys to check the eutectic temperature, curves were also run on compositions close to the end of the eutectic horizontal, in order to obtain some idea as to the apparent lowering of the eutectic temperature common to alloys in this range and these results, which are given later, are of interest in this connection. It was also hoped that this method would give a check on the location of the end of the eutectic horizontal which was obtained by another method. The latter method consisted of heating to just above the eutectic temperature and quenching a number of alloys in this range so that those containing even small amounts of the resolidified aluminum-silicon eutectic could be determined by means of microscopic examination. For the cooling curves, 200 g. samples were melted

⁹ E. H. Dix, Jr., and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans.* (1926) **73**, 560.

down in a small closed graphite crucible in the electric furnace used for preparation of the alloys, and the cooling rate adjusted to give a drop of 3° C. per min. just before reaching the eutectic temperature for near-eutectic alloys. The temperature was measured with a platinum, platinum-rhodium couple connected to a Leeds & Northrup type K potentiometer. The couple was protected with concentric tubes, an inner one of porcelain and an outer of graphite and was calibrated against the freezing point of aluminum and of the aluminum-copper eutectic, 548° C.

TABLE 1.—*Description of Aluminum-silicon Alloys**

M No.	Analysis			
	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Manga- nese, Per Cent.
822.....		0.03	0.27	
823.....		0.03	0.50	
824.....		0.03	0.73	
825.....		0.03	1.01	
826.....		0.03	1.25	
827.....		0.03	1.53	
828.....		0.03	1.81	
871.....		0.05	1.08	
872.....		0.05	1.98	
881.....		0.02	0.14	
882.....		0.02	0.36	
2011.....		0.04	1.41	
2012.....		0.04	1.70	
2013.....		0.04	2.00	
2014.....	0.02	0.04	2.87	
2015.....		0.06	4.98	
1395 (Slowly cooled).....			11.82	
2083 (Slowly cooled).....			12 Approximate	
578.....	0.02	0.03	0.87	0.01
581.....	0.02	0.04	2.07	0.01
585 (Al-Si Hardener).....	0.03	0.14	12.15	0.01
587 (Al-Si Hardener).....	0.03	0.18	18.02	0.01
1623 (Al-Si Hardener).....	0.01	0.18	18.99	
2028 (No. 22 gage sheet).....		0.02	0.06	
2029 (No. 22 gage sheet).....		0.02	0.14	
2030 (No. 22 gage sheet).....		0.02	0.16	
2031 (No. 22 gage sheet).....		0.02	0.23	

* All alloys chill cast in iron mold except as noted.

CHECKING EUTECTIC CONCENTRATION

In determining the eutectic concentration, 200 g. samples of several alloys of approximately the eutectic composition were melted down and cooled in the manner used for cooling curves, as previously described.

The resulting cylinder was then sectioned, polished and examined microscopically for all-eutectic areas. It was apparently almost impossible to produce a uniform eutectic structure over more than small areas, with even this slow rate of cooling; both primary aluminum and silicon would be found comparatively close together. An analysis of drillings from an area showing a small amount of primary aluminum gave a silicon

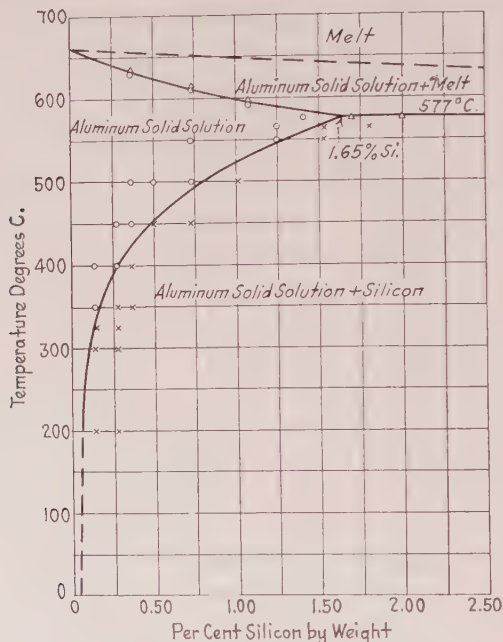


FIG. 1.—ALUMINUM END OF ALUMINUM-SILICON DIAGRAM, SHOWING THE RESULTS OF THIS INVESTIGATION.

content of 11.82 per cent. This was considered a satisfactory check on the value of 11.6 per cent. determined by Edwards¹⁰ using thermal methods and the 11.7 per cent. given by Gwyer and Phillips,¹¹ especially considering the great ease with which the aluminum-silicon structures become modified.

METHODS OF DETERMINING SOLUBILITY

The methods used for the solubility determinations were carried out as described in a previous paper.¹² In accordance with this procedure, all specimens were homogenized by annealing at 15 to 20° C. under the eutectic temperature for a week or more, after which the first tube of specimens was quenched; then the temperature was lowered in steps of

¹⁰ J. D. Edwards: *Op. cit.*

¹¹ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

¹² E. H. Dix, Jr., and H. H. Richardson: *Op. cit.*

20 to 30° C. and upon attaining the next quenching temperature the annealing was continued for a period of time which was longer the lower the temperature. The detailed procedure employed is given in Table 2. Heating at the lowest temperature, 200° C., was done in a fused salt bath using a bimetallic thermostat for temperature regulation and a small motor-driven stirrer for bath circulation. A Tycos recording thermometer recorded the bath temperature. The annealing periods at 200° C. ranged from a minimum of 1 week to a maximum of 18½ weeks. The former period proved to be insufficient. It was found that a period of about 3 weeks was required to give an indication of precipitation at that temperature, although longer annealing proved that equilibrium had not been reached in that time.

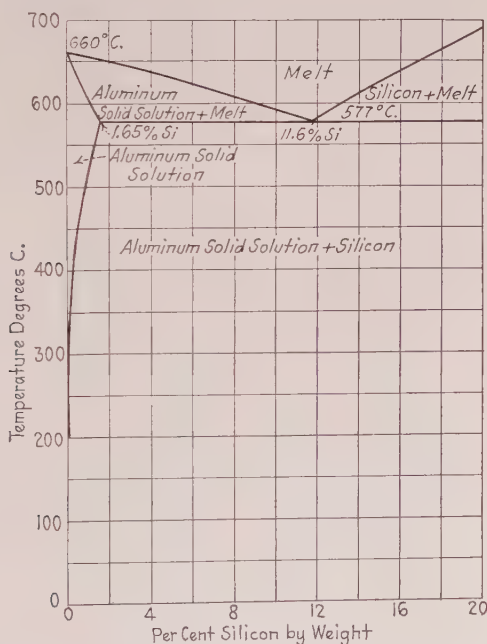


FIG. 1a.—ALUMINUM END OF ALUMINUM-SILICON DIAGRAM. LOCATION OF EUTECTIC AFTER EDWARDS AND LIQUIDUS CURVES AFTER GWYER AND PHILLIPS.

SOLIDUS DETERMINATIONS

Heating experiments to fix the point of intersection of the solubility curve and eutectic horizontal required a different type of annealing block from the one previously described. The construction is shown in Figs. 2 and 3. Fig. 2 is a view of the complete block, which was of cast aluminum and measured 10 by 10 by 12 in. The central part of the block was machined out to form three concentric hollow cylinders of progressively smaller diameters, the smallest, which was the actual heat-

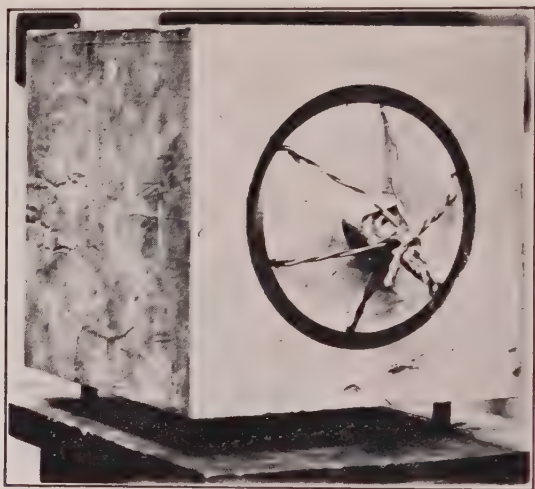


FIG. 2.—ANNEALING BLOCK USED FOR SOLIDUS DETERMINATIONS.



FIG. 3.—PLUG FOR ANNEALING BLOCK ILLUSTRATED IN FIG. 2, SHOWING ARRANGEMENT OF SPECIMENS AND THERMOCOUPLE WIRES.

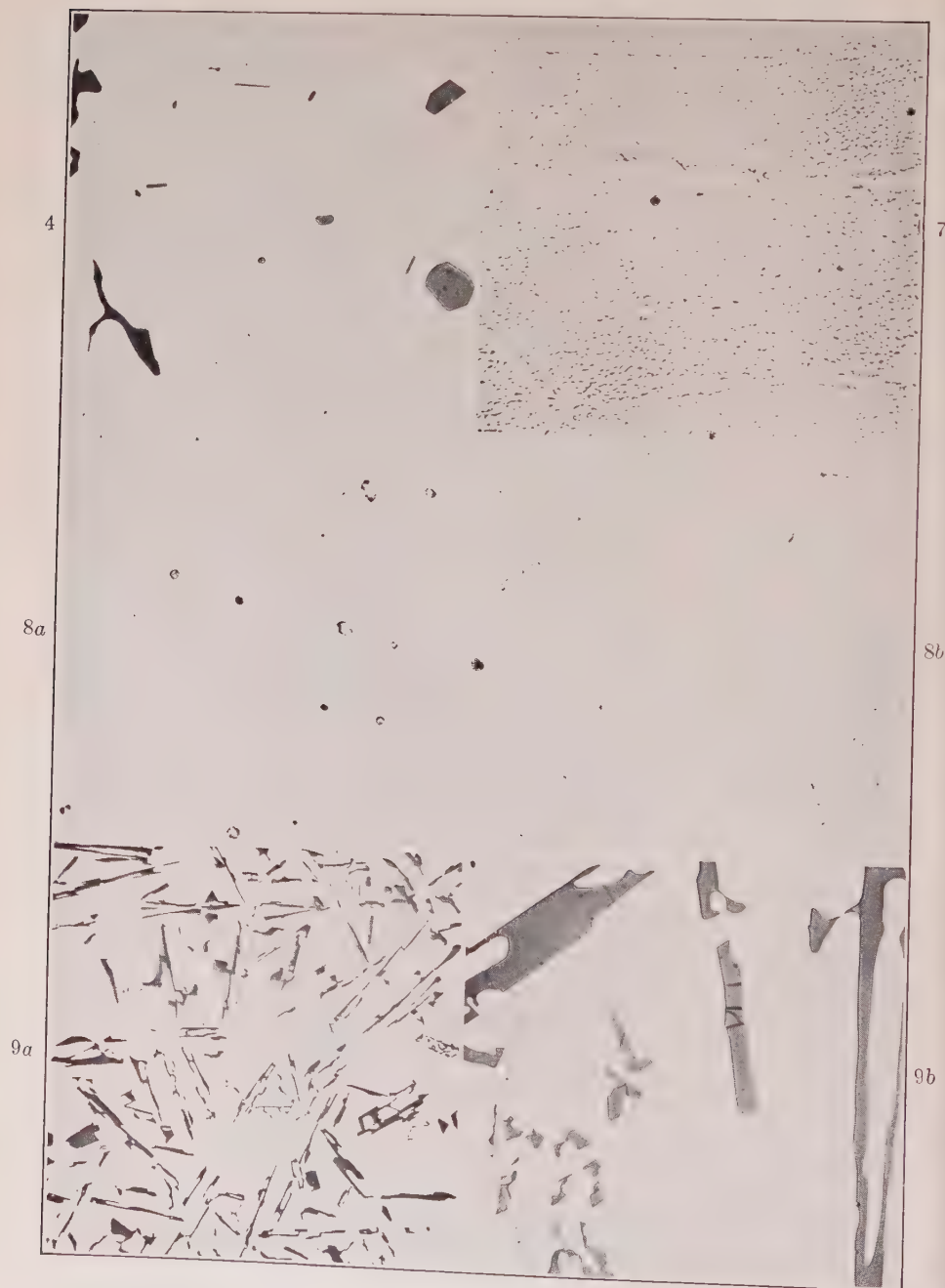
ing chamber, being located near the center of the block and measuring 2 in. in dia. and 2 in. in length. The aluminum plug shown in Fig. 3 was machined to fit these cylindrical recesses, and had six longitudinal grooves to take as many iron-constantan thermocouples, the hot junctions of which were peened into the specimens, as shown in the photograph. When the plug was in place in the block the specimens occupied the small 2 by 2-in. chamber. Quenching was accomplished by withdrawing plug, specimens, and couples, as a single unit. The block was heated in a Hoskins electric muffle furnace of interior dimensions 12 by 18 by 48 in. The furnace temperature was controlled by a Leeds & Northrup controller-recorder, and the whole arrangement was very similar to that described for annealing solubility specimens. With this block, temperature variations in the annealing chamber were reduced to a negligibly small value; furthermore, the temperature of the specimens could be accurately measured.

Details of the heat treatment of the solidus specimens are given in Table 2. All specimens were annealed for 120 hr. at 560° C. in order to produce equilibrium, and then quenched. Groups of specimens were reheated to about the eutectic temperature for a shorter time, after which the furnace temperature was increased to a point close to the desired temperature. The temperature was then raised by small increments to the desired point, and the specimens were quenched after at least 30 min. Temperature readings were taken at 5-min. intervals. The highest temperature recorded during the 30-min. period was taken as the annealing temperature. The specimens were then examined microscopically for evidence of melting.

IDENTIFICATION OF SILICON PARTICLES

The microscopic examination of the annealed specimens to determine the solid solubility of the silicon was a comparatively simple matter as long as the particles of constituent were fairly large, since the silicon could be easily recognized by its purple or slate color in the unetched condition.

Fig. 4 shows dark particles of silicon in the aluminum matrix in an alloy containing 1.53 per cent. silicon annealed 190 hr. at 565° C., cooled to 300° C., and quenched after 24 hr. at that temperature. Silicon stands between FeAl_3 and MnAl_3 in point of hardness and when polished with magnesia will appear flat in the matrix if proper pressure is used during polishing. With too light pressure it has a tendency to stand in relief and may at the same time become faded or otherwise discolored so that identification by color may not be reliable. The latter is especially apt to be true with small and scattered particles present. To remove surface flow a light swab with a $\frac{1}{2}$ per cent. aqueous solution of hydrofluoric acid produced a sharper particle definition, but long etching destroyed



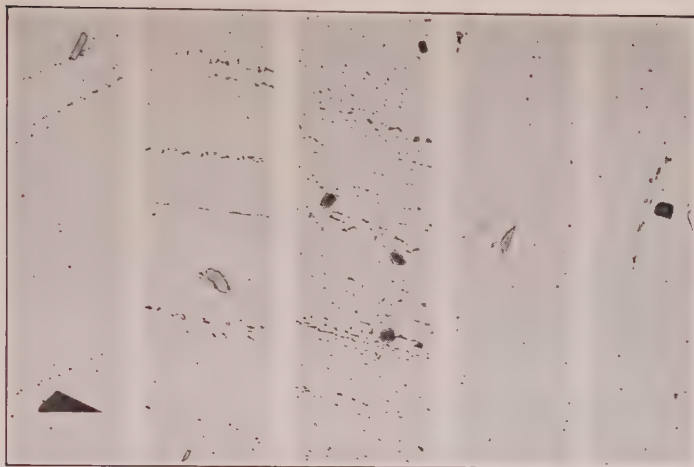


FIG. 5.—COMPOSITE PHOTOMICROGRAPHS DISTINGUISHING BETWEEN PARTICLES OF FE-SI CONSTITUENT AND SILICON IN ALUMINUM-SILICON ALLOYS. THE FINAL POLISHING OPERATION HAS BEEN OMITTED BECAUSE IT TENDS TO OBSCURE THE TONE CONTRAST. UNETCHED. $\times 500$. FROM LEFT TO RIGHT:

M No.	Silicon, Per Cent.	Quenching Temperature, Deg. C.	Remarks
823-450	0.50	450	Showing Si (dark) and an Fe-Si constituent.
823-450	0.50	450	Showing an Fe-Si constituent.
824-450	0.73	450	Showing silicon particles.
826-550	1.25	550	An Fe-Si particle.
827-550	1.53	550	Showing a silicon particle.

FIG. 4.—ALUMINUM-SILICON ALLOY (M 827-300) CONTAINING 1.53 PER CENT SILICON.

Chill cast in iron mold. Annealed 190 hr. at 565°C ., cooled to 300°C . in 214 hr., held 24 hr. and quenched. Unetched. $\times 500$. Shows dark silicon particles in the aluminum matrix, this amount of silicon being considerably in excess of the solid solubility at 300°C .

FIG. 7.—ALUMINUM-SILICON ALLOY No. 22 GAGE (0.025 IN.) SHEET CONTAINING 0.14 PER CENT. SILICON (M 2029).

Heated 13 hr. at 450°C ., 45 hr. at 495°C ., quenched and reheated 3100 hr. at 200°C . and quenched. Etched lightly with $\frac{1}{2}$ per cent. HF. $\times 500$. Shows a precipitate of silicon.

FIG. 8a.—CHILL CAST ALUMINUM-SILICON ALLOY CONTAINING 0.50 PER CENT. SILICON (M 823A). UNETCHED. $\times 500$. Shows fine "rosettes" of aluminum-silicon eutectic.

FIG. 8b.—CHILL CAST ALUMINUM-SILICON ALLOY CONTAINING 1.53 PER CENT. SILICON (M 827A).

Etchant, $\frac{1}{4}$ per cent. HF. $\times 500$. Showing typical network of aluminum-silicon eutectic produced by rapid chilling.

FIG. 9a.—ALUMINUM-SILICON ALLOY OF APPROXIMATELY THE EUTECTIC COMPOSITION (M 2083). UNETCHED. $\times 100$.

Slowly cooled in furnace. The micrograph shows a coarse eutectic structure with probably some excess aluminum areas.

FIG. 9b.—SPECIMEN OF FIG. 9a AT HIGHER MAGNIFICATION. UNETCHED. $\times 500$. The light colored β (Fe-Si) will be noted.

TABLE 2.—*Heat Treatment of Aluminum-silicon Alloys**A. Solubility Determination**First Anneal:*

M Nos. 822-8, 871-2, 881-2.

190 hr. at 565° C. and quenched.

190 hr. at 565° C. cooled to 500° C. in 24 hr., held 24 hr. and quenched.

190 hr. at 565° C. cooled to 400° C. in 168 hr., held 72 hr. and quenched.

190 hr. at 565° C. cooled to 300° C. in 214 hr., held 24 hr. and quenched.

Second Anneal:

M Nos. 825-6-7-8, 822-3, 881-2

168 hr. at 565° C. and quenched.

M Nos. 824-5-6-7-8, 871

168 hr. at 565° C., cooled to 550° C. in 28 hr. and quenched.

M Nos. 822-3-4-5, 881-2

168 hr. at 565° C., cooled to 450° C. in 76 hr., held 24 hr. and quenched.

M Nos. 881-2, 822-3-4.

168 hr. at 565° C., cooled to 350° C. in 124 hr., held 40 hr. and quenched.

Reheating:

M Nos. 822-3, 881-2.

168 hr. at 565° C. and quenched, reheated at 200° C. for 1 week, 10 days, 2 weeks, 3 weeks and 4 weeks.

M Nos. 822-3, 881-2.

Previously quenched from 350° C. and reheated at 325° C. for 144 hr. and quenched.

M Nos. 2028-9, 2030-1.

13 hr. at 458° C., 45 hr. at 495° C. and quenched.

Reheated 3100 hr. at 200° C. and quenched.

Maximum Solubility by Reheating:

M Nos. 2011-2-3-4-5.

Heated to 574.5° C. in 142.5 hr., held 55 min. and quenched.

Heated to 577° C. in 101 hr., held 55 min. and quenched.

M Nos. 2011-2-3.

Heated to 576° C. in 122 hr., held 30 min. and quenched.

B. Solidus Determination

M Nos. 824, 882, 871.

120 hr. at 560° C. and quenched, then reheated.

M No. 824.

43.5 hr. at 577° C., raised to 606.5° C. in 1½ hr., held at least 30 min., and quenched. Same procedure for other temperatures, 608°, 610°, 614.5°, 618.5° and 620° C.

M No. 882.

45 hr. at 577° C., raised to 627.5° C. in 1½ hr. and quenched after at least 30 min. Same procedure for other temperatures, 629.5°, 634°, 637.5°, 640° C.

M No. 871.

21 hr. at 577° C., raised at 589° C. in 1 hr. and quenched after at least 30 min. Same procedure for other temperatures, 589°, 592°, 599.5°, 600.5° C.

the color. Silicon particles are remarkably resistant to most etching reagents, and they generally are not attacked except for possible outlining or fading in color.

The identification of small silicon particles was made more difficult by the inevitable presence of the Fe-Si¹³ constituents, and could be accomplished only when a comparison of constituents was possible in the same field of the microscope.

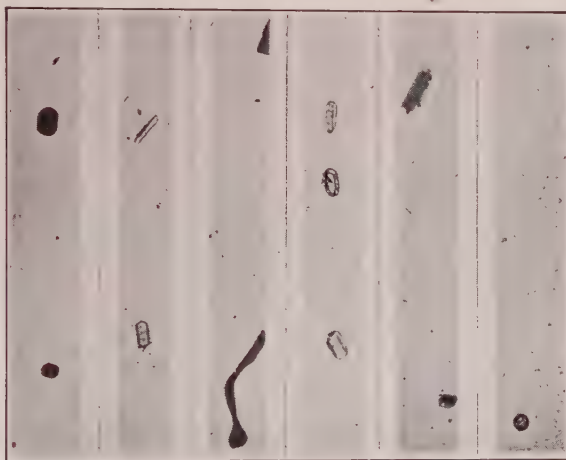


FIG. 6.—COMPOSITE PHOTOMICROGRAPHS OF ALUMINUM-SILICON SOLUBILITY SPECIMENS REPRESENTING POINTS ON EITHER SIDE OF THE SOLUBILITY CURVE. UN-ETCHED. $\times 500$. FROM LEFT TO RIGHT:

M No.	Silicon, Per Cent.	Quenching Temperature, Deg. C.	Remarks
827-565	1.53	565	Shows silicon particles.
826-565	1.25	565	Shows no silicon.
825-500	1.01	500	Shows silicon particles.
824-500	0.73	500	Shows no silicon.
882-400	0.36	400	Shows silicon particles.
822-400	0.27	400	Shows no silicon.

A photographic method was used to aid in distinguishing between the silicon particles and the particles of iron-silicon constituent when particles of only one constituent occurred in a given field of the microscope. This method consists of making a number of exposures on a single plate by screening off all light except a narrow slot, and by moving an adjustable negative holder a distance approximately equal to the width of this slot for each exposure. Fig. 5 shows how readily the par-

¹³ This symbol is used to denote a ternary body of aluminum, iron and silicon, see page 180.

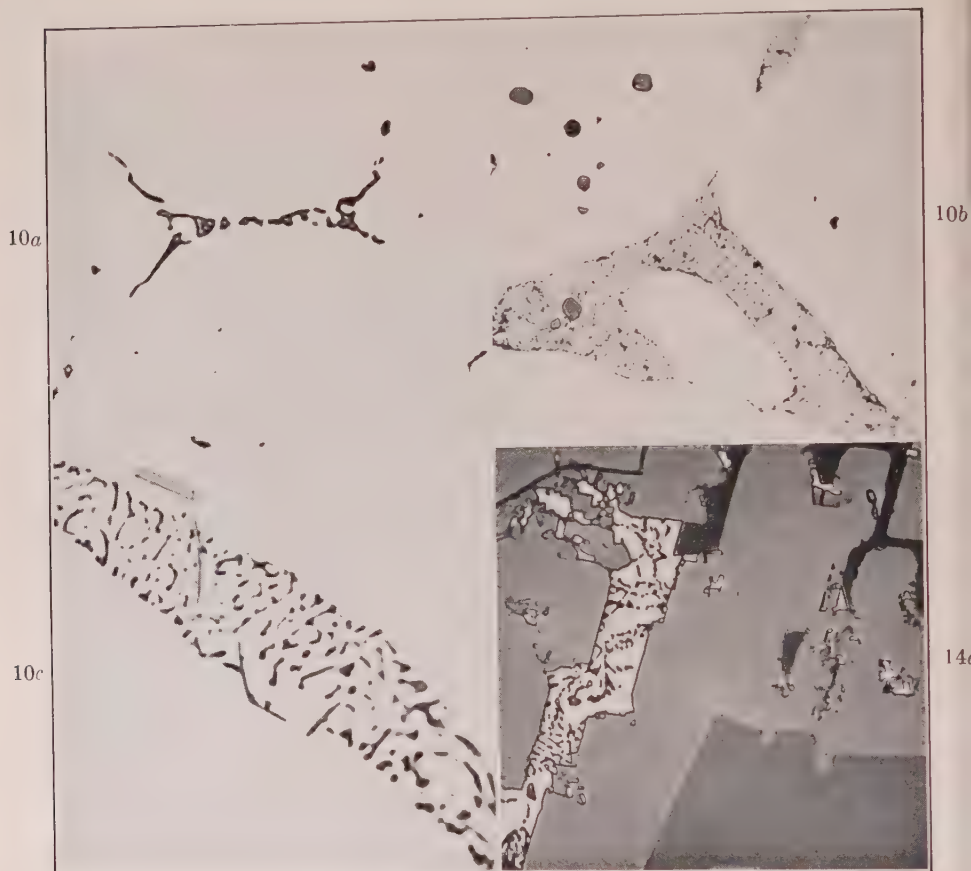


FIG. 10a.—CHILL CAST ALUMINUM-SILICON ALLOY CONTAINING 1.08 PER CENT. SILICON (M 871-A-603).

Annealed 141 hr. at 577° C., temperature increased to 595° C. and held 30 min.; specimen quenched. Unetched. $\times 1500$. Particles of silicon at the grain boundaries due to heating above the solidus.

FIG. 10b.—CHILL CAST ALUMINUM-SILICON ALLOY CONTAINING 2.87 PER CENT. SILICON (M 2014-577).

Annealed 24 hr. at 385° C., 26 hr. at 510° C., 24 hr. at 550° C., 20 hr. at 566° C., temperature increased to 577° C. in 5+ hr., held 30 min. or more, and specimen quenched. Etchant, $\frac{1}{2}$ per cent. HF. $\times 500$. Fine aluminum-silicon eutectic due to resolidification of melted areas, and larger silicon particles.

FIG. 10c.—CHILL CAST ALUMINUM-SILICON ALLOY CONTAINING 1.70 PER CENT. SILICON (M 2012-577.)

Same heat treatment as specimen of Fig. 10b. Unetched. $\times 1500$. Fine aluminum-silicon eutectic and light-colored needles of β (Fe-Si).

FIG. 14a.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 28.09 PER CENT. IRON AND 28.87 PER CENT. SILICON (M 2090). $\times 500$.

Etched 45 sec. with 25 per cent. HNO_3 at 70° C. and quenched. This alloy lies at the intersection of the lines Al-FeSi₂ and FeAl₃-Si (see Fig. 11). White aluminum, dark particles of silicon, an aluminum-silicon eutectic and two unknown constituents may be noted.

ticles in different specimens can be compared in this way. The difference in tone which seems quite evident in the photograph is too slight to be readily distinguished visually when the particles are widely separated or in different specimens. Fig. 6 is given as a matter of record to illustrate observations on both sides of the solubility curve.

SOME TYPICAL STRUCTURES

A finely-dispersed precipitate produced by a solution heat treatment and quenching followed by reheating at 200° C. for 3100 hr. is shown in Fig. 7. The alloy contained 0.14 per cent. silicon. Two chill cast structures are shown in Figs. 8a and 8b; the alloys contain respectively 0.50 and 1.53 per cent. silicon. A comparison of Figs. 8a and 7 will

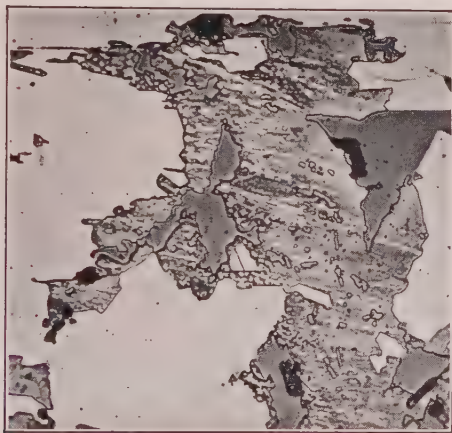


FIG. 14b.—SPECIMEN OF FIG. 14a (M 2090-560) ANNEALED 2 WEEKS AT 560° C. $\times 500$.

Etched 10 sec. with $\frac{1}{2}$ per cent. HF. Annealing has caused the disappearance of aluminum from the microstructure. The smooth, dark particles are silicon, but the other two phases are unknown.

show that a considerable quantity of silicon was retained in solid solution by fast chilling. Slowly cooling an alloy containing approximately 12 per cent. silicon produced the structure shown in Figs. 9a and 9b. The light-colored Fe-Si constituent will be noted in both micrographs.

Specimens heated and quenched for the solidus determination were polished and examined microscopically for evidence of melting. This was indicated by grain boundary melting or a cast eutectic structure occurring at the grain boundaries. Fig. 10a shows the effect of heating a 1.08 per cent. silicon alloy 2 or 3° C. above the solidus and quenching. The resolidified aluminum-silicon eutectic in a 2.87 per cent. silicon alloy is shown in Fig. 10b. The eutectic, which is not resolved at this magnification, surrounds the larger dark particles of excess silicon. An alloy containing 1.70 per cent. silicon, which was given the same heat treatment as that of Fig. 10b, is shown at a higher magnification in Fig. 10c.

RESULTS FROM COOLING CURVES

Cooling curves of several alloys gave the following results:

M No.	Silicon, Per Cent.	Eutectic Arrest, Deg. C.
585	12.15	576.9
	Approximate 6.0	577.9
872	1.98	577.6 to 575.4
828	1.81	573.4 to 571.4
827	1.53	571.4 to 569.5

The curves on the three low-silicon alloys were taken largely as a matter of interest to determine the lowest concentration of silicon giving a perceptible eutectic arrest. In the last two alloys the degree of undercooling combined with the small amount of eutectic freezing was sufficient to prevent the entire mass from reaching the eutectic temperature.

MODIFIED DIAGRAM

Fig. 1 shows the results of this part of the investigation plotted on an enlarged scale, while Fig. 1a shows a larger portion of the aluminum end of the aluminum-silicon diagram, in which the eutectic point has been located after Edwards¹⁴ and the liquidus curves after Gwyer and Phillips.¹⁵ The solidus was found to be slightly convex downward. The determination of the shape of the solidus apparently has not been made by other investigators.

A comparison of the solubility limits, as determined in this and other investigations, can be obtained from the following tabulation:

Solubility, Percentage Silicon					
Temperature, Deg. C.	Otani ¹⁶	Gwyer and Phillips ^{17*}	Köster and Müller ^{18*}	Bosshard ¹⁹	Dix and Heath
577		1.60	1.69	1.50-1.60	1.65
550	1.45	1.35	1.57		1.30
500		0.90	1.17		0.80
450	0.95 (460° C.)		0.83		0.48
400			0.50		0.29
350	0.52 (360° C.)		0.25		0.17
300			0.10	<0.20	0.10
200					0.05

* Scaled from curve.

¹⁴ J. D. Edwards: *Op. cit.*

¹⁵ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

¹⁶ B. Otani: *Op. cit.*

¹⁷ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

¹⁸ W. Köster and F. Müller: *Op. cit.*

¹⁹ M. Bosshard: *Op. cit.*

The close agreement with the results of Köster and Müller is a matter of some surprise since the annealing time used by these experimenters was not nearly as long as the authors have found to be necessary to produce equilibrium and further, the method of chemical analysis is known to be unreliable as an exact indication of the amount of dissolved and free silicon. This fact is readily shown by an analysis of the results in Table 4 of their paper, in which the amount of silicon obtained as SiO_2 (which is taken by them to indicate the amount of dissolved silicon) after annealing at 350°C. , varies from 0.28 to 0.90 depending on the total silicon content.

PART II.—ALUMINUM-IRON-SILICON ALLOYS

The constitution of aluminum-iron-silicon alloys has been investigated and discussed by several authors with more or less thoroughness. The complexity of the system is generally acknowledged and rapid progress toward a clear conception of the equilibrium relations has been hindered thereby. The constitution of the aluminum end of the aluminum-iron system is comparatively simple. Iron and aluminum form the compound FeAl_3 , which forms a eutectic with aluminum, at 1.7 per cent. iron, and 655°C. ²⁰ The solubility of FeAl_3 in aluminum is practically nil. The difficulty in developing the ternary system is due to the possible occurrence of ternary compounds or solid solutions, the identities of which are extremely obscure. The first discovery of the existence of a constituent in commercially pure aluminum, which was neither FeAl_3 nor Si, was reported in 1919 by Merica, Waltenberg and Freeman.²¹ Another investigator, Wills,²² the same year described an unknown constituent in addition to FeAl_3 .

An account of a systematic study of the aluminum-iron-silicon alloys containing up to 8 per cent. each of iron and silicon appeared in the Eleventh Report to the Alloys Research Committee of the Institution of Mechanical Engineers.²³ The theory there advanced was that the constituent "X" was a product of a reaction taking place between the melt and FeAl_3 , which had first separated as part of a binary complex. Photomicrographs and thermal analysis data were offered in support of this theory.

²⁰ E. H. Dix, Jr.: A Note on the Microstructure of Aluminum-iron Alloys of High Purity. *Proc. A. S. T. M.* (1925) **25**, 120.

²¹ P. D. Merica, R. G. Waltenberg and J. R. Freeman: Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium. *Trans.* (1920) **64**, 3, and *Bur. Standards Scientific Paper* No. 337 (1919).

²² L. J. Wills: Micrography of Aluminum Alloys. *The Metal Industry.* (British) (Nov. 21, 1919).

²³ W. Rosenhain, S. L. Archbutt and D. Hanson: *Op. cit.*

More recently one of the present authors²⁴ has discussed the constituents occurring in aluminum of commercial purity. Gwyer and Phillips²⁵ have discussed the constituents and phase relations in the aluminum-iron-silicon alloys for a particular rate of cooling of 8° C. per min. Their results were represented by the method used by Rosenhain, Archbutt and Hanson.

The equilibrium relations in aluminum-iron-silicon alloys are at once so complex and important and information on them is so comparatively meager, that it was felt that any further data would be exceedingly desirable, and this investigation was accordingly undertaken. The original purpose was to identify the unknown constituents, determine the composition, or limits of composition, and to locate the boundaries of the various phase fields below the surfaces of crystallization.

An isothermal section of the aluminum part of the ternary model has been drawn and the various phases indicated. The existence of the compound FeAl_3 in the binary system aluminum-iron has been confirmed. Two other constituents in the ternary system, in addition to silicon and aluminum, have been recognized and their respective fields indicated. These have been designated as $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$, in conformity with the general scheme suggested in a previous paper.²⁶ These symbols are intended to suggest that these two ternary bodies consist of aluminum, iron and silicon and are probably more nearly of the nature of a solid solution than a definite chemical compound.

PREPARATION OF AL-Fe-Si ALLOYS

In addition to the lot of pure aluminum (M1932, see page 166 for analysis) used in the first part of the investigation a lot of 99.2 per cent. grade was used. This was possible for some alloys because the principal impurities were the alloying elements and the effect of copper and manganese in small amounts was negligible. The analysis of the lot follows:

M No.	ALUMINUM, BY DIFFERENCE PER CENT.	COPPER, PER CENT.	IRON, PER CENT.	SILICON, PER CENT.	MANGANESE, PER CENT.
1540	99.22	0.05	0.37	0.35	0.01

The same lot of silicon was used in this part of the investigation as in Part I. The analysis is given on page 166.

Iron was added in the form of Armeo wire of the following composition as determined by analysis:

M No.	IRON BY DIFFERENCE, PER CENT.	COPPER, PER CENT.	SILICON, PER CENT.	MANGA- NESE, PER CENT.	CARBON, PER CENT.	PHOS- PHOROUS, PER CENT.	SULFUR PER CENT.
345	99.895	0.042	0.005	0.022	0.013	0.005	0.018

²⁴E. H. Dix, Jr.: Observations on the Occurrence of Iron and Silicon in Aluminum. *Trans.* (1923) **69**, 957.

²⁵A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

²⁶E. H. Dix, Jr., and W. D. Keith: The Etching Characteristics of Constituents in Commercial Aluminum Alloys. *Proc. A. S. T. M.* (1926) **26**, No. 2.

Alloys (Table 3) low in iron and silicon were prepared and cast in the same manner as the aluminum-silicon alloys, Part I, by the process of adding iron and silicon hardeners to pure aluminum. Alloys containing 22 per cent. or more of iron and a maximum of half as much silicon were melted in small Acheson graphite crucibles in an improvised electric resistor furnace which was capable of attaining a temperature estimated to be 1500° C. Aluminum was first melted down and silicon then added as the pure element. The iron was added as Armco iron wire, and the charge of a total of 700 g. was heated for some time, often as long as an hour, to dissolve all the iron in the melt. After brief stirring, a sample for analysis and bars of the dimensions previously given were cast, as described in Part I.

TABLE 3.—*Description of Aluminum-iron-silicon Alloys**

M No.	Analysis	
	Iron, Per Cent.	Silicon, Per Cent.
2090	28.09	28.87
2091	0.48	19.40
2092	2.02	17.60
2093	3.94	15.61
2094	5.79	13.82
2095	7.29	11.77
2096	9.74	9.90
2097	11.88	7.67
2098	13.84	5.65
2099	15.06	7.54
2100	16.82	1.85
2101	19.34	0.58
2102	6.89	13.95
2033	2.92	11.90
2034	4.84	10.80
2035	16.74	13.51
2036	15.22	2.43
2037	15.10	5.71
2334	22.42	6.61
2335	25.38	12.71
2336	29.49	14.78
2346	31.65	3.47
2347	35.91	3.95
2509	40.78	0.03 C 0.05
2339	33.12	16.58

* All alloys chill cast in iron mold.

Cooling curves were taken on a few alloys of widely separated compositions to determine the maximum safe annealing temperature that could be used without danger of partial melting taking place. The melting

point of the aluminum-silicon eutectic, 577°C ., seemed to be the upper limit, although an arrest was noted at 567°C . in alloys of low iron and silicon contents. This was obviously the result of the freezing of only a very small amount of eutectic, as noted in Part I.

All annealing for equilibrium work was carried out at 560°C ., in order to make the results of annealing different sets of alloys comparable. The equipment used for the aluminum-silicon solubility determination and described in Part I, was employed. The principal difficulty lay in obtaining equilibrium and consequently the annealing periods ranged from 1 to 5 weeks, depending upon the iron and silicon content. Even after 5 weeks, equilibrium did not appear to have been attained in some alloys, particularly those which were very porous. Incidentally, porosity and cracks were quite characteristic of alloys containing considerable amounts of iron and relatively less silicon.

The authors' first attempt to solve the problem was made with alloys containing up to 2 per cent. each of iron and silicon. Comparison and differentiation of constituents in these alloys was complicated by small particle size and similarity in their appearance both in the etched and unetched conditions, although no difficulty was experienced in recognizing silicon with the usual exception of very small particles.

GUERTLER METHOD OF MAPPING TERNARY DIAGRAMS

After an exhaustive examination did not yield conclusive results it was decided to attempt to obtain some general information concerning this system, following Dr. Guertler's method²⁷ of mapping out ternary diagrams, and using alloys containing larger percentages of both iron and silicon, so that the constituents could be more easily identified.

In 1926, Dr. K. L. Meissner²⁸ presented a paper before the American Institute of Mining and Metallurgical Engineers in which he indicated how Dr. Guertler's method may be applied to the ternary system aluminum-iron-silicon, basing his diagram on a preliminary paper by one of the authors.²⁹ The data were admittedly insufficient for this purpose, but served to explain the general plan of attack. A little later the authors had opportunity to discuss the whole scheme in considerable detail with Dr. Guertler on the occasion of his visit to this country. They have attempted to follow his plan of attack, but have encountered many difficulties which perhaps are not so apparent on the surface.

The method is based on the fact that if binary or ternary homogeneous bodies occur then they will form among themselves and the three components various ternary systems, subdividing the original model, or

²⁷ W. Guertler: Considerations in Theoretical Metallurgy. *Metal. u. Erz.* (1920) **17**, 192.

²⁸ K. L. Meissner: The Microstructure of Aluminum. *Trans.* (1926) **73**, 622.

²⁹ E. H. Dix, Jr.: *Op. cit.*

triangle, considering an isothermal section, into a number of smaller triangles, the apices of which coincide with the compositions of the compounds and the components. Passing from a field included in the area of one of these smaller triangles into an adjacent field will result in the disappearance of one constituent from the microstructure and the appearance of a new one. The location of the boundary line can then be determined by microscopic examination and the compositions of the phases will lie along these lines. The two articles referred to should be consulted for a more thorough explanation of this method. Its application to the aluminum-iron-silicon system is illustrated in Fig. 11.

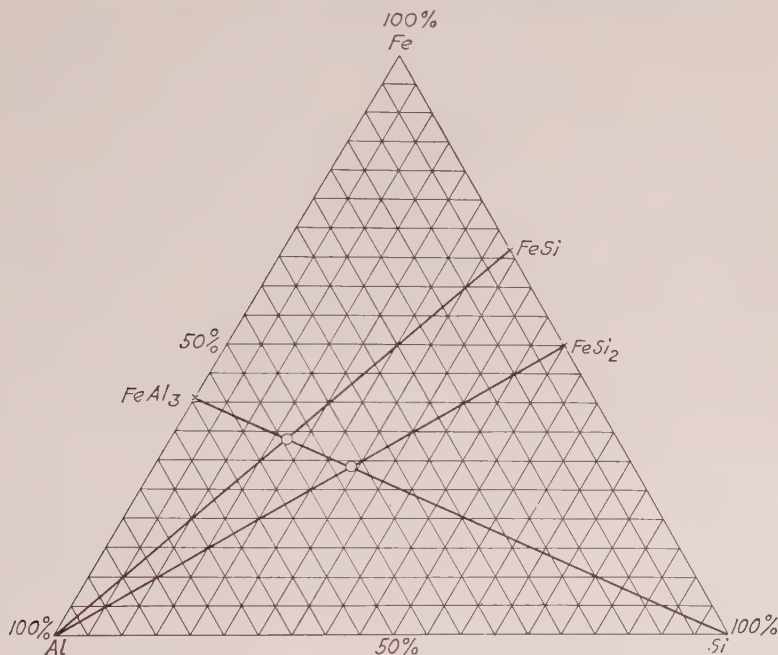


FIG. 11.—AL-Fe-Si DIAGRAM OF POSSIBLE QUASI-BINARY SYSTEMS.

APPLICATION OF GUERTLER METHOD

The existence of two iron-silicon binary phases of variable compositions corresponding approximately to the formulae FeSi and FeSi_2 has been established by Phragmen³⁰ by means of X-ray analysis and microscopic examination. These two compounds and FeAl_3 are indicated in Fig. 11, and lines representing possible quasi-binary systems have been drawn, assuming that no ternary phases occur. To determine which of the lines, if any, was real, alloys were prepared corresponding to the intersections of the lines as shown by the circles. The microstructure of

³⁰ G. Phragmen: Constitution of the Iron-Silicon Alloys. *Jnl. Iron Steel Inst.* (1926); also *Engineering* (1926) **122**, 369.

the alloy at the intersection of Al-FeSi_2 and $\text{FeAl}_3\text{-Si}$ is shown in Figs. 14a and 14b. Fig. 14a, chill cast, shows the white aluminum, a fine aluminum-silicon eutectic, larger dark particles of silicon and two unknown constituents. The structure of a portion of the same specimen, after being annealed 2 weeks at 560°C . is shown in Fig. 14b. The structure shown is representative of the alloy and illustrates as nearly as possible the relative amounts of the three phases present, none of which is aluminum. The presence of three phases shows that the point does not lie on a quasi-binary line and the absence of aluminum is further proof that the line Al-FeSi_2 does not exist.

The alloy corresponding to the intersection of the lines Al-FeSi and $\text{FeAl}_3\text{-Si}$, after being annealed for 5 weeks at 560°C . is illustrated in Fig. 15. Three phases were distinguished and no silicon or aluminum found. The presence of the three phases shows that this point also does not lie on a quasi-binary line and the absence of aluminum is additional proof that the line Al-FeSi does not exist and likewise the absence of silicon confirms the conclusion that the line $\text{FeAl}_3\text{-Si}$ is not real. This conclusion is contrary to the findings of Fuss³¹ quoted by Meissner, which were to the effect that the line $\text{FeAl}_3\text{-Si}$ does correspond to a real quasi-binary line.

TERNARY PHASE OR PHASES IN STRUCTURE OF ALUMINUM-RICH ALLOYS

The experiments apparently gave fairly good evidence that the microstructure of aluminum-rich alloys was complicated by the existence of at least one ternary phase. The next step, therefore, was to prepare alloys lying along the line of 80 per cent. aluminum, as shown in Fig. 12. After being annealed at 560°C . they were examined microscopically both etched and unetched. The work of comparison and differentiation of the microconstituents proved to be the most difficult of the entire investigation. Without going into a detailed account of the first microscopic examination, the presence of two quasi-binary lines seemed to be indicated. One of these, marked "B" in Fig. 12 was sharply defined by the appearance or disappearance of silicon in the microstructure, according as the quantity of silicon in the alloy was increased or decreased. The position of the second line was rather doubtful because of the difficulty of distinguishing FeAl_3 from the $\alpha(\text{Fe-Si})$ constituent. The line is marked "A" in Fig. 12.

Following out the original plan, alloys with compositions lying along the lines A and B were cast and annealed. Some of them were extremely hard and brittle, as well as porous. The results of microscopic examination of these alloys were somewhat disappointing from the standpoint of locating any homogeneous ternary phases, but served one very important

³¹ Vincenz Fuss: The Constitution of Ternary Aluminum Alloys. *Ztschr. f. Metallkunde* (Jan., 1924) 16, 24.

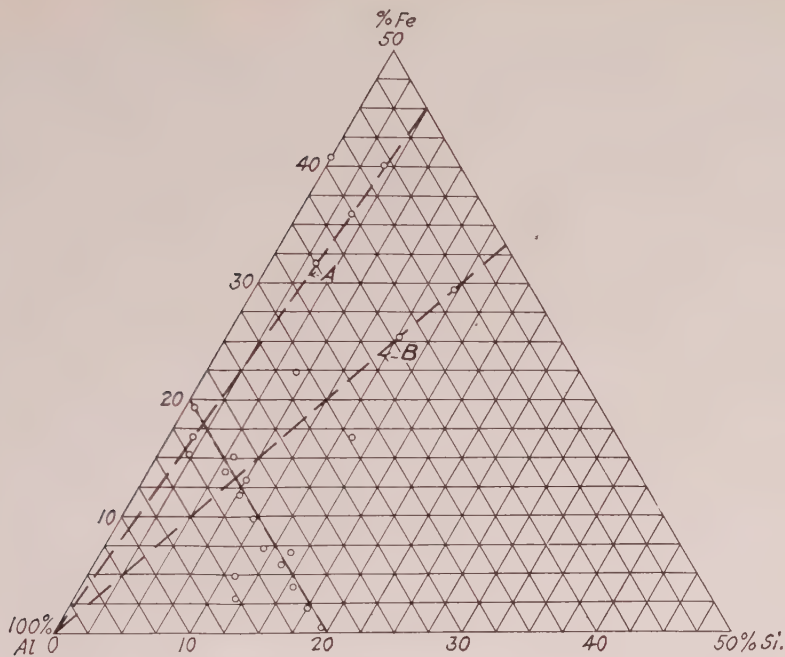


FIG. 12.—DIAGRAM SHOWING COMPOSITIONS OF AL-FE-SI ALLOYS.

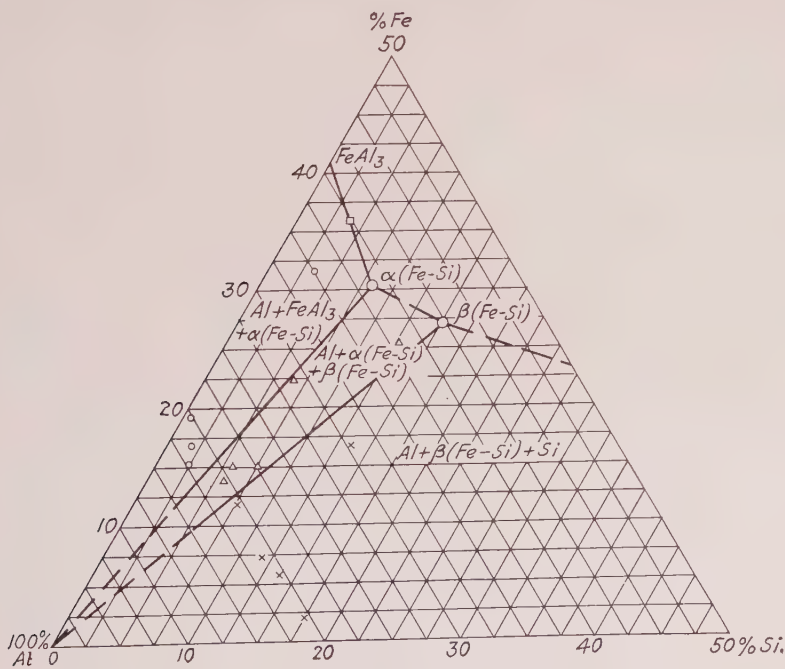


FIG. 13.—AL-FE-SI PHASE FIELDS AT 560° C.

purpose, namely, to locate the points on these lines at which free aluminum was no longer visible in the microstructure.

DIFFICULTY OF LOCATING PHASE FIELD BOUNDARIES

After an intensive metallographic examination of the alloys the diagram shown in Fig. 13 has been drawn in a manner which appears to be most easily reconciled with the authors' observations. The unknown phases are designated respectively as α (Fe-Si) and β (Fe-Si) and their compositions are shown by the large circles to indicate possible variable compositions. These points are located for the sake of completeness from theoretical and other considerations, and should not be construed as being supported by conclusive evidence except in so far as the presence or absence of free aluminum was shown by alloys located on the lines *A* and *B* as mentioned above. There are thus three fields which have aluminum as a common constituent in the microstructure and so are of particular importance in the metallography of aluminum.

It should be realized that the aluminum undoubtedly holds small amounts of some of the other constituents in solid solution. No attempt has been made to determine or even indicate the extent of the aluminum

FIG. 15.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 33.12 PER CENT. IRON AND 16.58 PER CENT. SILICON (M 2339-560).

Annealed for 5 weeks at 560° C. and quenched. Etched 40 sec. with 25 per cent. HNO_3 at 70° C. $\times 500$. This alloy lies at the intersection of the lines Al-FeSi and FeAl_3 -Si (see Fig. 11) and shows three unknown phases. The dark areas are due to porosity and cracks.

FIG. 16.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 16.82 PER CENT. IRON AND 1.85 PER CENT. SILICON (M 2100-560).

Annealed for 2 weeks at 560° C. and quenched. Etched 40 sec. with 25 per cent. HNO_3 at 70° C. $\times 500$. Shows the field aluminum plus FeAl_3 plus α (Fe-Si). (See Fig. 13.) Cores of particles are FeAl_3 ; they are in relief. α (Fe-Si) is lighter in color.

FIG. 17.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 15.22 PER CENT. IRON AND 2.43 PER CENT. SILICON (M 2036-560).

Annealed 2 weeks at 560° C. and quenched. Etched 10 sec. with 20 per cent. H_2SO_4 at 70° C. $\times 500$. This alloy lies in the same field as the specimen shown in Fig. 16. Also shows core of FeAl_3 blackened by the etch and α (Fe-Si) which is less severely attacked.

FIG. 18.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 15.10 PER CENT. IRON AND 5.71 PER CENT. SILICON (M 2037-560).

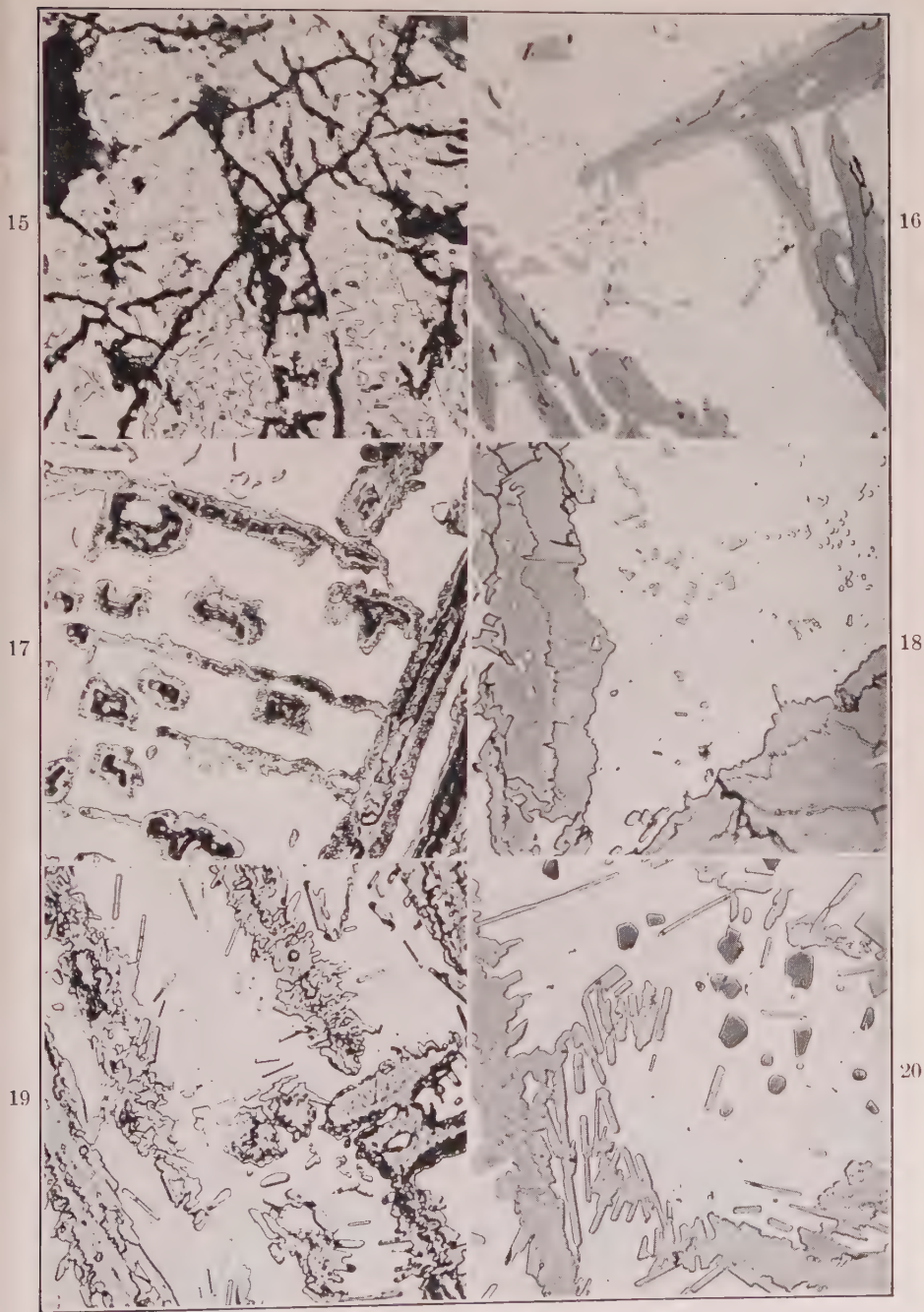
Annealed 2 weeks at 560° C. and quenched. Etched 40 sec. with 25 per cent. HNO_3 at 70° C. $\times 500$. The alloy lies in the field aluminum plus α (Fe-Si) plus β (Fe-Si). (See Fig. 13.) Shows two large particles consisting of α (Fe-Si) and β (Fe-Si), also smaller particles which are probable β (Fe-Si).

FIG. 19.—SAME SPECIMEN AS SHOWN IN FIG. 18.

Etched 10 sec. with 20 per cent. H_2SO_4 at 70° C. $\times 500$. Showing the effect of 20 per cent. H_2SO_4 on α (Fe-Si) and β (Fe-Si). They seem to be attacked about equally. The significance of the blackened areas is doubtful.

FIG. 20.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 11.88 PER CENT. IRON AND 7.67 PER CENT. SILICON (M 2097-560).

Annealed 2 weeks at 560° C. and quenched. Etched 40 sec. with 25 per cent. HNO_3 at 70° C. $\times 500$. This alloy lies in the field aluminum plus β (Fe-Si) plus silicon. (See Fig. 13.) The dark silicon particles will be readily distinguished. The large particles seem to consist of both α (Fe-Si) and β (Fe-Si). The smaller needles are undoubtedly β (Fe-Si).



solid solutions. Starting from the iron side of the aluminum corner, the first field encountered is aluminum plus FeAl_3 plus $\alpha(\text{Fe-Si})$. An alloy lying in this field is shown in Fig. 16. The dark cores are considered to be FeAl_3 and are in relief, although a dark or light appearance is often a matter of focus. The amount of the $\alpha(\text{Fe-Si})$ produced by adding 1.85 per cent. silicon to an alloy containing 16.82 per cent. iron is quite remarkable. The question of proof as to which part of the duplex particles is FeAl_3 seems to be answered satisfactorily in Fig. 17. The alloy lies in the same phase field and contains 15.22 per cent. iron and 2.43 per cent. silicon. It was etched with 20 per cent. sulfuric acid at 70° C., which is known to blacken FeAl_3 . The cores of the particles in Fig. 17 are quite consistently blackened.

With increasing silicon content FeAl_3 should disappear and the new phase should be $\beta(\text{Fe-Si})$. This situation is shown in Fig. 18. The specimen was etched the same as that of Fig. 16. The marked similarity in the appearance of $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$ will be evident. Most of the small particles appear to be $\beta(\text{Fe-Si})$. The duplex nature of the large needles is only made known by the fact that one part, $\alpha(\text{Fe-Si})$, stands in relief with respect to the other.

The same alloy etched with 20 per cent. sulfuric acid at 70° C. is shown in Fig. 19. $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$ are attacked about equally by this etch. A few black areas will be noted, the significance of which is doubtful. The field aluminum plus $\beta(\text{Fe-Si})$ plus silicon is illustrated in Fig. 20, which is an annealed alloy containing 11.88 per cent. iron and 7.67 per cent. silicon. The dark particles of silicon will be readily recognized. In Fig. 20, however, both $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$ are shown together, in addition to aluminum and silicon. This is only an example of the difficulty involved in the exact location of the phase field boundaries. The alloy lies close to the boundary, but the presence of appreciable amounts of silicon shows that it lies within the field $\text{Al}-\beta(\text{Fe-Si})-\text{Si}$ and the presence of $\alpha(\text{Fe-Si})$ must be attributed to failure to obtain equilibrium.

It might be suspected that equilibrium would be more rapidly attained the greater the amount of the soluble constituent, silicon. Figs. 21*a* and 21*b* are micrographs of an alloy in which the iron and silicon contents are the reverse of the alloy of Fig. 20, thus placing the composition well within the field $\text{Al}-\beta(\text{Fe-Si})-\text{Si}$. They are respectively unetched and etched with 20 per cent. sulfuric acid at 70° C. The dark particles in both micrographs are silicon and the needles are the homogeneous $\beta(\text{Fe-Si})$.

REACTION ZONES

One of the most striking characteristics of the microstructure of these ternary alloys is the occurrence of reaction zones around the iron-silicon

constituents. This has led several investigators to suggest that FeAl_3 which forms at a relatively high temperature reacts with some of the liquid to form the so-called "X" constituent. One of the authors has previously shown³² that in certain aluminum alloys containing comparatively large amounts of iron and silicon several reaction zones are often found around a single needle presumably of FeAl_3 . The scope of the present investigation has not permitted a study of changes taking place during solidification of the alloys. The theory advanced in the Eleventh Report to the Alloys Research Committee³³ has already been mentioned. It has been endorsed and considerably amplified by Gwyer and Phillips,³⁴ who, however, made no attempt to obtain equilibrium by annealing and consequently encountered several unstable phases in addition to the equilibrium structure. That such reaction can be produced by long-time annealing at a high temperature is shown by a comparison of Figs. 16 and 22. In the chill cast alloy of Fig. 22 the reaction zone around the large needles of FeAl_3 is very narrow in comparison with that shown in Fig. 16, in which the width of the zone has been considerably increased by annealing for 2 weeks at 560°C . The "Chinese script" figures seem to be the same as $\alpha(\text{Fe-Si})$ by tone comparison. These reaction zones and the resulting constituents of nearly identical color and hardness, which give very similar results on etching, have been the cause of the great difficulty in establishing the constitution of this system.

THE COMPOUND FeAl_3

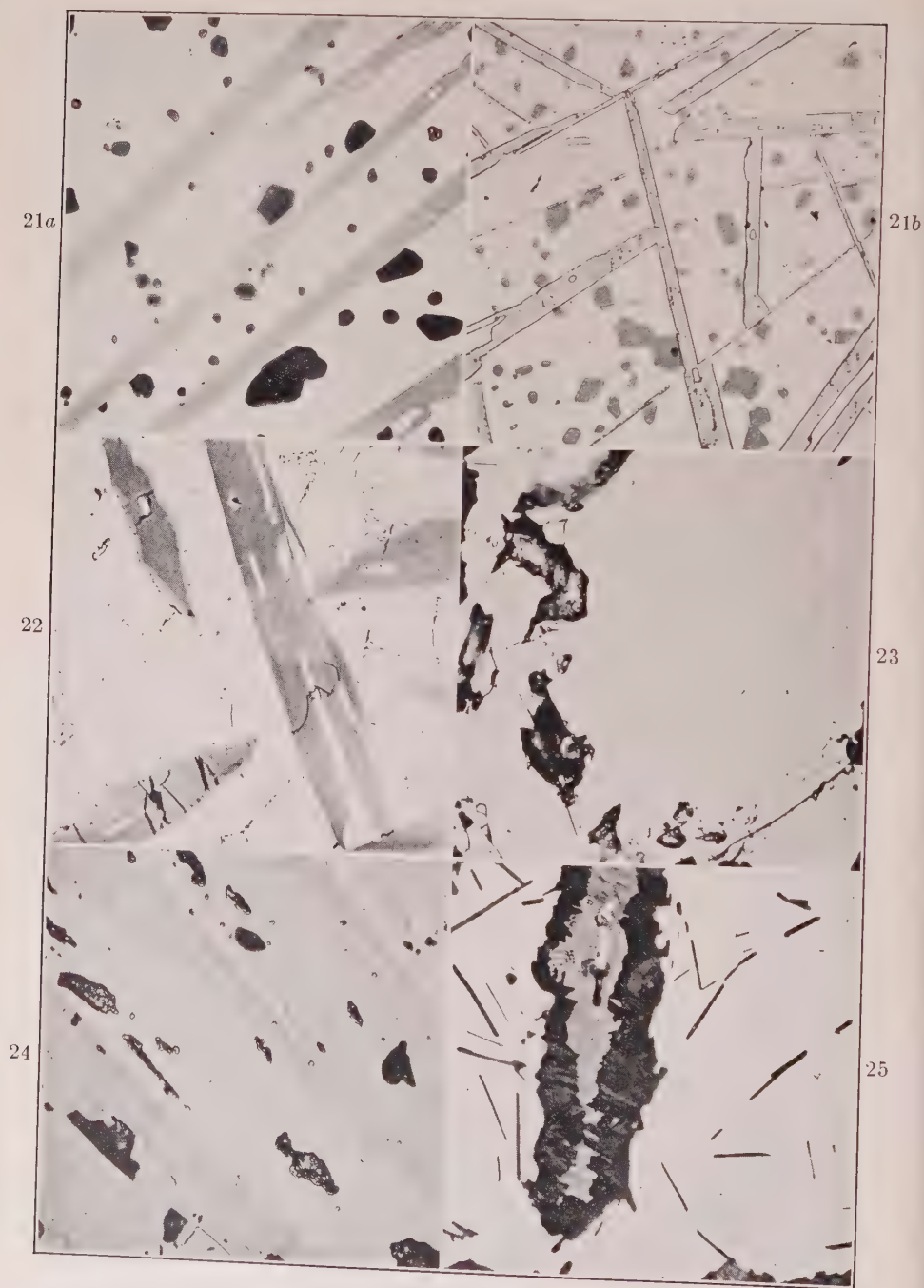
To confirm the existence of the binary compound FeAl_3 , an alloy corresponding to its composition was prepared. Fig. 23 is a photomicrograph of the alloy after annealing 2 weeks at 560°C . It is completely homogeneous. The black areas are holes and cracks. The actual composition of this alloy is very close to the theoretical percentage of the compound. The 25 per cent. nitric acid quench has slightly darkened the compound. It was thought that this alloy would be useful in trying different etches for purposes of the identification of FeAl_3 ; actually it was not, on account of non-uniform results, and the different behavior of the constituent when alone and in the presence of other constituents.

The diagram of Fig. 13, shows a line drawn from FeAl_3 intersecting a line from the aluminum corner at a point which theoretically should be the composition of $\alpha(\text{Fe-Si})$. In other words FeAl_3 and $\alpha(\text{Fe-Si})$ should form a quasi-binary system and any alloy lying upon this line should consist of these two constituents. Fig. 24 shows the unetched microstructure of the annealed alloy lying on this line. It contains 35.91 per cent. iron and 3.95 per cent. silicon. The two phases should be FeAl_3

³² E. H. Dix, Jr.: *Op. cit.*

³³ W. Rosenhain, S. L. Archbutt and D. Hanson: *Op. cit.*

³⁴ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*



and $\alpha(\text{Fe-Si})$. The drawing of the line is further justified because alloys lying on the side toward the aluminum corner contain free aluminum and those on the other do not. The dotted line, $\alpha(\text{Fe-Si})$ - $\beta(\text{Fe-Si})$ also represents this important change in the microstructure.

ETCHING REAGENTS

Two etching reagents were used for the most part—25 per cent. nitric acid at 70° C. followed by quenching in cold water and 20 per cent. sulfuric acid at 70° C., likewise followed by quenching in cold water. Often, however, the quenching was omitted and the specimen merely held in a stream of cool water without appreciably affecting the results. The etching times were usually 40 sec. with 25 per cent. nitric acid and 10, 20 or 30 sec. with 20 per cent. sulfuric acid. The nitric acid quench was most desirable for photographic purposes, not attacking the aluminum matrix and slightly improving the contrast of the other constituents, at the same time not severely attacking them. The action of 20 per cent. sulfuric acid on all constituents except silicon was rather severe; $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$ were attacked about equally, both being roughened, but not darkened much. Sulfuric acid was used to identify FeAl_3 which is colored black, but the particles were not attacked equally, the degree being influenced by both particle size and depth of surface flow by polishing. Fifteen seconds etching with $\frac{1}{2}$ per cent. hydrofluoric acid was

FIG. 21a.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 7.29 PER CENT. IRON AND 11.77 PER CENT. SILICON (M 2095-560).

Annealed 2 weeks at 560° C. and quenched. Unetched. $\times 500$. Shows silicon and homogeneous needles of $\beta(\text{Fe-Si})$.

FIG. 21b.—SPECIMEN OF FIG. 21a.

Etched 10 sec. with 20 per cent. H_2SO_4 at 70° C. and quenched. $\times 500$. Shows a uniform attack on needles of $\beta(\text{Fe-Si})$. The color of the silicon particles seems to have faded by etching.

FIG. 22.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 16.82 PER CENT. IRON AND 1.85 PER CENT. SILICON (M 2100).

Unetched. $\times 500$. Shows large particles of FeAl_3 surrounded by a narrow sheath of $\alpha(\text{Fe-Si})$. The "Chinese script" figures appear to be $\alpha(\text{Fe-Si})$.

FIG. 23.—CHILL CAST ALUMINUM-IRON ALLOY, CONTAINING 40.78 PER CENT. IRON (M 2509-560).

Annealed 2 weeks at 560° C. and quenched. Etched 40 sec. with 25 per cent. HNO_3 at 70° C. $\times 500$. This alloy corresponds to the composition of FeAl_3 . Shows the compound FeAl_3 , which has not been attacked by the etch, except for a slight darkening. The black areas are holes.

FIG. 24.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 35.91 PER CENT. IRON AND 3.95 PER CENT. SILICON (M 2347-560).

Unetched. $\times 500$. This alloy lies on the line FeAl_3 - $\alpha(\text{Fe-Si})$. (See Fig. 13.) Annealed 22½ days at 560° C. and quenched. Shows the two phases FeAl_3 (dark), $\alpha(\text{Fe-Si})$ and black holes.

FIG. 25.—CHILL CAST ALUMINUM-IRON-SILICON ALLOY CONTAINING 13.84 PER CENT. IRON AND 5.65 PER CENT. SILICON (M 2098-560).

Annealed 2 weeks at 560° C. and quenched. Etched 20 sec. with $\frac{1}{2}$ per cent. HF. $\times 500$. The alloy lies in the field aluminum plus $\alpha(\text{Fe-Si})$ plus $\beta(\text{Fe-Si})$. $\alpha(\text{Fe-Si})$ has been roughened, but not darkened by the etch. $\beta(\text{Fe-Si})$ has been colored nearly black; it is somewhat overetched.

fairly satisfactory for identifying $\beta(\text{Fe-Si})$ which was colored brown. This etch did not seem to attack $\alpha(\text{Fe-Si})$, as shown in Fig. 25. The alloy contains 13.84 per cent. iron and 5.65 per cent. silicon and was annealed 2 weeks at 560°C . The small needles and outer parts of duplex particles are $\beta(\text{Fe-Si})$ colored dark brown, and the cores of $\alpha(\text{Fe-Si})$ are not colored, although they are roughened. Five and 10 per cent. sodium hydroxide were also tried, but with no particular success for identification of constituents.

EFFECT OF ANNEALING ON THE "AS CAST" STRUCTURE

The "as cast" structure, particularly the elongated prismatic bodies of FeAl_3 and $\beta(\text{Fe-Si})$, was not obliterated to any great extent by annealing. Duplex particles found in the unannealed alloys were generally in a state of metastable equilibrium, and annealing caused an increase in the amount of one constituent and a decrease in the amount of the other. The "Chinese script" formation exhibited a remarkable persistency in retaining its original form during annealing. The aluminum-silicon eutectic was commonly found in all cast alloys irrespective of composition. Upon annealing, however, the silicon either disappeared entirely or coalesced into larger particles, depending upon the composition. As pointed out previously, $\beta(\text{Fe-Si})$ usually appeared in the microstructure as needles, the size of which seemed to depend on the rate of cooling. Apparently the sensitivity to the cooling rate is extraordinarily great as even in a bar of section $1\frac{1}{2}$ by $\frac{5}{8}$ in. cast in an iron mold the structure was found to be very different as between the outer part, which is the first to freeze, and the center.

BOUNDARY OF THE $\text{Al-}\beta(\text{Fe-Si})\text{-Si}$ PHASE FIELD

Bosshard has furnished an interesting confirmation of the boundary of the aluminum- $\beta(\text{Fe-Si})$ -silicon phase field. In the paper³⁵ previously referred to he gives the results of a series of electrical conductivity measurements made upon some alloys containing a constant quantity of silicon (1 per cent.) and increasing quantities of iron. These show that after annealing at 550°C . the conductivity increased with increase in iron up to 2 per cent. iron and then gradually decreased. Concerning this phenomenon he states: "From these conductivity investigations it is to be expected that iron and silicon neutralize each other in the atomic relationship of 1:1 and in the weight relationship of 2:1. This chemical compound does not seem to be ferro-silicon, but apparently a ternary compound exists which contains iron, silicon and aluminum."

According to the isothermal section (560°C .) of Fig. 13, aluminum-iron-silicon alloys containing 1 per cent. silicon and less than 1.75 per

³⁵ M. Bosshard: *Op. cit.*

cent. iron fall in the field aluminum- β (Fe-Si)-silicon. The scope of this investigation has not permitted the determination of the solubility of the silicon in aluminum under these conditions, but some solubility undoubtedly exists. Thus in Bosshard's experiments the addition of iron to the 1 per cent. silicon alloys caused the formation of β (Fe-Si) and so removed some of the silicon from solution, thus increasing the conductivity. This effect continued until further addition of iron caused the alloys to enter the aluminum- α (Fe-Si)- β (Fe-Si) phase field, whereupon the conductivity began to decrease, since the effect of the increasing amount of insoluble constituent was no longer overbalanced by the greater effect of removing a constituent from solution.

In concluding this discussion the authors desire to reconcile the previously published information on this system and the facts which are everyday knowledge to those familiar with the microstructure of commercially pure aluminum and its alloys with the observations made in this investigation.

"X" CONSTITUENT OF COMMERCIAL ALUMINUM

It is common knowledge that there occurs in aluminum of commercial purity a light gray constituent which definitely is not FeAl_3 and therefore must be due to the simultaneous presence of aluminum, iron and silicon. It was first designated as the "X" constituent by Merica and his associates.³⁶ The very characteristic structure aptly described by Wills³⁷ as "Chinese script" is apparently the eutectic form of this constituent. Commercial use of the aluminum-silicon alloys has led to the general knowledge that the iron-silicon constituent occurring in these alloys takes the form of curved needles or plates, although in other ways it is difficult to distinguish from the iron-silicon constituent which occurs when there is no free silicon in the microstructure. The "Chinese script" structure has never been observed associated with free silicon. These facts alone would seem to indicate the existence of two iron-silicon constituents. However, the diagrams given in the Eleventh Report to the Alloys Research Committee indicate a single constituent, also designated as "X", existing both in the aluminum of commercial purity and the aluminum-silicon alloys. It has already been stated³⁸ by one of the authors of that report that they were not satisfied that the system had been completely worked out.

Gwyer and Phillips³⁹ show a number of constituents in each field owing to incomplete equilibrium, but follow Rosenhain in indicating the

³⁶ P. D. Merica, R. G. Waltenberg and J. R. Freeman: *Op. cit.*

³⁷ L. J. Wills: *Op. cit.*

³⁸ Discussion by W. Rosenhain of paper, "Observations on Occurrence of Iron and Silicon in Aluminum," by E. H. Dix, Jr. *Trans.* (1923) **69**, 971.

³⁹ A. G. C. Gwyer and H. W. L. Phillips: *Op. cit.*

existence of "X" in both the high and the low-silicon alloys. It has seemed to the present authors that the continuance of the designation "X" in view of our more complete knowledge of the system would be ill-advised and hence they have followed a new and more logical terminology. Thus the low-silicon aluminum-iron-silicon constituent generally occurring as "Chinese script" in cast commercial aluminum designated as "X" by Merica, Rosenhain and Gwyer and their associates is indicated as $\alpha(\text{Fe-Si})$ in the diagram of Fig. 13, and the second aluminum-iron-silicon constituent containing more silicon as $\beta(\text{Fe-Si})$. This is the constituent occurring as curved needles or plates associated with the silicon particles in the commercial aluminum-silicon alloys. This structure is probably the ternary eutectic mentioned by Gwyer and Phillips who have given its freezing point as 577°C . and its composition as 11.6 per cent. silicon, 0.8 per cent. iron and 87.6 per cent. aluminum, although they name its constituents as silicon, aluminum and "X".

Needles are also formed in commercial ingot aluminum containing a relatively large amount of iron in comparison with the silicon, but these are FeAl_3 and have definitely different etching characteristics from $\beta(\text{Fe-Si})$. The existence of a phase field containing only FeAl_3 and aluminum could not be proved. Even a small amount of silicon caused the formation of considerable $\alpha(\text{Fe-Si})$.

ACKNOWLEDGMENTS

The authors desire to express their appreciation to G. W. Wilcox for the development and printing of the negatives and to H. V. Churchill under whose direction the chemical analyses were made.

DISCUSSION

P. D. MERICA, New York, N. Y.—This paper is another contribution by Mr. Dix and his collaborators to the metallography of aluminum, and it is now evident that it is one of a series of investigations of a systematic nature devoted to the metallography of aluminum. I want to congratulate the authors and company not only on the execution of its work but on the conception of the plan.

This method of attacking the metallography of alloy systems is somewhat new. We all know that in the past we have had to search the literature for information on the constitution of alloys and such as we could find was pretty well scattered around.

The older investigations have been done in a variety of laboratories, with widely varying methods, accuracy and dependability, and although these early investigations gave us a perspective of the situation, they left a great many features undecided and were often wanting in accuracy necessary for a practical application of their results.

It is certainly very gratifying to note the distinct difference in method today, in which certain laboratories are devoting themselves with accuracy and precision to the working out of the practically useful features of the constitutional diagrams and with the accuracy that is requisite for the practical application of that knowledge.

In the second part of this paper the authors deal with the metallography of alloys containing both iron and silicon, and particularly with the constitution of the so-called

"X" constituent. I have a particular interest in this part of the paper since I had the honor of rendering the tremendous service to metallography of recognizing that we did not know anything about this constituent and of therefore calling it "X." And I note that one of the conclusions of the paper has been to eliminate the "X" in this situation, replacing it by two Greek letters. But those two Greek letters are not so ominous as they sound because although the "X" constituent meant nothing, since its composition was unknown, the two alpha and beta constituents that Mr. Dix has christened really are known, as a result of his investigations to within rather narrow limits. He has made a distinct contribution to the elucidation of this mysterious puzzle.

There is another feature of the paper which is of general interest, and that is the application of Dr. Guertler's method of metallographic attack to ternary systems. Mr. Dix's paper is well worth reading from that standpoint alone, as an excellent illustration of the application of this method and as an indication of its power in determining the metallography of ternary systems.

In the first place, we should perhaps not overestimate the profundity of nature of this method, the basis of which is really very simple. As nearly as I understand it, it consists in this one premise, that if in a ternary system you prepare a series of alloys lying along any straight line in the ternary graphical diagram as commonly made, and examine the structure of these alloys along that line and find two constituents, and only two; and that if you make enough of those alloys so that you can find two alloys at either end, each of which has only one constituent and that constituent one of the two which you have been observing along that line, then on that line you have a so-called pseudobinary system. But I do not think we can draw the conclusion that if you study the structure of an alloy on some such straight line in a ternary diagram and find only two constituents, it necessarily follows that those are the two constituents at the ends of that line on the ternary diagram. That is *probably* true, but I do not think it is necessarily true any more than in a binary system you might assume that if you find two constituents they are necessarily the end components of the binary system. They may very well be instead intermetallic compounds.

We should remember that the basis of this method is a fairly simple one and it has its limitations, of which we must be very careful.

Then there is another feature of it that has somewhat puzzled me, and that is the effect of the presence of solid solutions on the application of the method. Certainly if you consider a ternary system, in which two of the metals form a continuous series of solid solutions, it is no longer true that the ternary diagram can be broken up into triangles as Dr. Guertler suggests, within each of which you will have three constituents, represented by composition of the corners of the triangle. In fact, in such a system you will have the ternary diagram broken up into four-sided figures in that case, of which one constituent will be a solid solution of unknown composition which you will not be able to determine by application of the method.

Furthermore, if we have limited solubility in a ternary system, there are difficulties introduced. Thus consider a ternary system, consisting of the metals *A*, *B* and *C*, of which the metal *C* is soluble to a limited extent in *A* and the metal *B* is not soluble in *A*, and a compound *BC*. If you consider the pseudobinary line joining the constituent *A* with the compound *BC*, assuming now for the moment that there is a solubility of constituent *C* in *A*, a point on that line according to the simple theory should consist of two constituents, the metal *A* and the compound *BC*. But you either have to assume that because of the presence of *BC* there can be no metal *C* dissolved in *A* in order for the point to line on that line and have only two phases, or you would find two constituents solely, not on the line joining *A* and *BC*, but on a line lying a little bit aside from it due to the displacement of that line by the solubility of *C* in *A*.

I do not think that the solid solubility effect applies to any extent in the work done by Mr. Dix as solubility of iron and silicon in aluminum is very slight, but it seems to me it can affect the application quite substantially in cases of solubility as great as 4 or 5 per cent.

S. L. HOYT, Schenectady, N. Y. —Possibly the designation by the authors of these ternary compounds, $\alpha(\text{Fe-Si})$ and $\beta(\text{Fe-Si})$, will not confuse anyone who is actively engaged in this particular series, aluminum-iron-silicon, but it is extremely confusing to me. When I look on a ternary diagram and see $\alpha(\text{Fe-Si})$, that indicates a compound of iron and silicon and particularly the alpha modification of that compound. The $\beta(\text{Fe-Si})$ would mean the beta modification of that same compound. It occurs to me that the designation the authors use here is unfortunate in that respect, and I am wondering if they can not think up some better way to pin down Dr. Merica's "X" constituent.

A second comment is that the determination of the surface of this ternary system should help the authors considerably in elucidating the constitution of these alloys. They have not used the ordinary thermal analysis for this. Possibly they intend to do that in the future. At any rate, Gwyer and Phillips have made quite a thorough thermal analysis of these alloys and it would be very interesting to make use of their results and apply them here.

A. C. HEATH, JR.—With regard to the nomenclature which we have used in referring to the ternary constituents, the placing of a hyphen between Fe and Si distinguishes the symbol from the ordinary chemical formula, and hence it is not intended to be indicative of definite chemical compounds. Incorporation of the symbol for aluminum in this designation would seem to make rather an unwieldy combination; its absence should not be a source of confusion to those familiar with the metallography of aluminum.

With regard to the occurrence of solid solutions in the ternary system and their effect on the application of Dr. Guertler's method, we appreciate fully the limitations pointed out by Dr. Merica but, as he has stated, they do not seem to have entered in particularly in this investigation.

Dr. Hoyt has suggested that thermal analysis would have been exceedingly useful. It was not our intention to conduct an elaborate investigation of this system, and the scope to which we limited ourselves did not appear to justify a resort to this method.

H. A. ANDERSON, New York, N. Y. (written discussion).—This survey of another portion of the aluminum-rich alloy field will be welcomed by all metallurgists interested in these light alloys. The investigations of Mr. Dix and his associates are accumulating information which serves as a guidebook for other workers in this field. The 1926 paper of Messrs. Dix and Keith on The Etching Characteristics of Constituents in Commercial Aluminum Alloys together with the contributions of Mr. Dix to the A. S. T. M. standard methods of metallographic testing have proved of great value to the writer.

Equilibrium relations in aluminum-silicon alloys are of particular interest at the present time in view of the attention that is being paid to the silicon alloys because of their corrosion resistance and suitability for die casting. The quality of the photomicrographs accompanying the discussion is in accordance with the high standards which have characterized other papers by the senior author and his associates. The evidence of photomicrographs regarding the boundaries of the various phase zones may be more generally studied by other investigators than the generally published cooling curves.

It is to be regretted that even these excellent photomicrographs cannot reproduce the degree of toning and slight color effect which form the basis for certain of the

authors' conclusions. These conclusions are probably amply justified by actual observation of the specimens through the microscope with the additional information thus obtainable, as is noted in the paragraph on etching reagents. An example of this type is illustrated in Fig. 14*b* where the authors conclude that none of the three phases present is aluminum. This difficulty of reproduction has been cleverly minimized in the composite photographs which permit comparisons of tones with identical photographic manipulations.

E. H. DIX, JR. and A. C. HEATH, JR.—The authors desire to emphasize that the primary object of the work on the ternary system aluminum-iron-silicon was to obtain data to aid in the identification of the constituents formed by these elements in aluminum and its commercial alloys. Naturally, they adopted the method that seemed to give the greatest promise of achieving this result with a minimum expenditure of time. In this respect the Guertler method proved of the greatest aid; in another system it may be quite useless. To have completely worked out the detailed constitution of this system would have required more time than conditions permitted, since many other problems were pressing. It is hoped to continue work on this system as time permits. However, it is felt that sufficient information has been gained to aid, in the meantime, in the interpretation of the structures encountered in practice. The work of Gwyer and Phillips mentioned by Dr. Hoyt has been studied with great interest, but any attempt to correlate these two researches would require more space than is available in this discussion.

After very careful consideration the authors are still of the opinion that the nomenclature proposed for designating the ternary constituents is more satisfactory than any other that has occurred to them, or that has been suggested in several discussions of the subject. Each class of alloys required some distinctive designations. We use α and β to designate two different solid solutions of zinc in copper in the brasses and Upton⁴⁰ has used $\gamma(C)$ to represent the solid solution of carbon in gamma iron. Surely our designation is no more difficult to accept than such terms as austenite, martensite, etc., used in steel metallography. The formation of ternary constituents, all of which contain aluminum, is quite general; thus, a ternary constituent of aluminum, manganese, and silicon has been proved, which according to our nomenclature would now be designated as $\alpha(\text{Mn-Si})$ and that of aluminum, iron, and copper as $\alpha(\text{Fe-Cu})$, and if at a later date other ternary constituents are discovered in these systems, then they would be designated as $\beta(\text{Mn-Si})$ and $\beta(\text{Fe-Cu})$, respectively. Our nomenclature has the advantage that it can be readily used to designate the various constituents which occur in the complicated commercial alloys. Thus, while it would be entirely feasible when describing the Al-Fe-Si system to specifically refer to the two ternary constituents as merely α and β solid solutions, yet in a complicated alloy where a number of such constituents due to other added elements are present this would result in considerable confusion which could only be prevented by many explanatory phrases.

⁴⁰ G. B. Upton: *The Structure and Properties of the More Common Materials of Construction*. New York, 1916. John Wiley & Sons, Inc.

Heat Treatment of Aluminum-silicon Alloys

By R. S. ARCHER,* L. W. KEMPF* AND D. B. HOBBS,† CLEVELAND, OHIO

(Detroit Meeting, September, 1927)

SILICON is one of the most important elements in the metallurgy of aluminum. It is always present in small amounts in the ordinary grades of "pure" aluminum, and hence in all alloys made therefrom. Within the last few years binary alloys containing up to 13 per cent. of silicon have come into extensive use for castings. Silicon is also added, beyond the amount present as an impurity, in alloys containing one or more other elements such as copper, manganese, magnesium and nickel.

The binary aluminum-silicon alloys are not yet heat treated to any extent in commercial practice, although, as will be shown, their properties are affected to a very considerable degree by heat treatment. There are other aluminum alloys that develop higher strength, but the special characteristics of the silicon alloys may well lead to the application of heat-treating processes on a commercial scale.

The role of silicon in the heat treatment of aluminum alloys is more important than would be indicated by consideration of the binary alloys alone, because many of the alloys that are heat treated in regular commercial practice contain some silicon in addition to that derived from the aluminum ingot as an impurity. Among these may be mentioned the heat-treated 195 alloy castings, and the wrought alloys 25S, Special 17S and 51S of the Aluminum Co. of America, and the German wrought alloy, Lantal.

It is the purpose of this paper to present the results of experimental work and the conclusions derived therefrom regarding the heat treatment of the binary aluminum-silicon alloys. The products heat treated included forgings, chill castings and both "normal" and "modified" sand castings.

REVIEW OF LITERATURE

The literature on the heat treatment of aluminum-silicon alloys is not very extensive. The following review gives the principal references of which the authors are aware, in which appreciable information may be found.

* Research Bureau, Aluminum Co. of America.

† Technical Department, The U. S. Aluminum Co.

It has been observed that in the annealing of cold-rolled aluminum sheet, slightly higher strengths may be obtained after annealing at relatively high temperatures, such as 500° C., than after annealing at relatively low temperatures, such as 300° C. This has been attributed by Gwyer and Rosenhain, with probable correctness, to a heat treatment effect involving silicon.¹

The improvement of the ductility of aluminum-silicon alloy castings is described by Zay Jeffries and R. S. Archer² as follows: "For example, a chill-cast test bar of an alloy containing about 10 per cent. silicon and no copper showed a tensile strength around 30,000 lb. per sq. in. and an elongation of about 7.5 per cent. in 2 in. After heating at 560° C. for 40 hr., followed by quenching, the tensile strength was about 27,500 lb. per sq. in., but the elongation was found to have increased to 21 per cent." This improvement was associated with a change in the form of the silicon particles.

Guillet describes the hardening of commercial aluminum by rapid cooling from high temperatures and attributes the effect to silicon.³ Two materials (apparently in the form of wires) were heat-treated with the results shown in Table 1.

TABLE 1.—*Effect of Quenching on Properties of Commercial Aluminum (Guillet)*

Treatment	Alloy I Silicon, 0.89 Per Cent.; Iron, 0.91 Per Cent.			Alloy II Silicon, 0.16 Per Cent.; Iron, 0.13 Per Cent.		
	T.S.	E	R	T.S.	E	R
Annealed at 450° C. 15 min.....	13,750	47.8	2.97	11,320	38.2	2.80
Air-cooled from 500° C.....	17,930	39.2	3.31	12,600	30.9	2.82
Quenched in water from 500° C.....	18,650	33.3	3.23	13,100	31.8	2.80

T. S. = tensile strength in lb. per sq. in.

E = percentage elongation.

R = electrical resistivity in microhms/cm.²/cm.

Guillet concludes: "In summary, the mechanical properties and the resistivity of commercial aluminum are modified by the speed of cooling, at least if the silicon content is somewhat elevated. The strength may increase by 40 per cent. and the elongation may decrease by 30 per cent. The resistivity, if the silicon attains 0.2 per cent., may be augmented at a maximum by 10 per cent.

¹ H. C. H. Carpenter and L. Taverner: Discussions on The Effects of Heat at Various Temperatures on the Rate of Softening of Cold-rolled Aluminum Sheet. *Jnl. Inst. Metals* (1917) **18**.

² U. S. Patent 1508556, filed Jan. 4, 1921; issued Sept. 16, 1924.

³ L. Guillet: Influence of the Speed of Cooling on the Properties of Commercial Aluminum. *Comptes Rendus* (June 16, 1924) **178**, 2081.

"The properties of quenched commercial aluminum are not appreciably modified by time."

It has been shown by D. B. Hobbs that modified sand-cast aluminum-silicon alloys can be hardened by quenching shortly after solidification; that is, during the initial cooling of the casting.⁴ This effect, which is evidently analogous to that of heat treatment, will be described in detail in this paper.

Daniels has described experiments on the heat treatment of normal sand-cast alloys containing up to about 5 per cent. silicon with about 0.3 to 0.4 per cent. iron.⁵ The tensile test specimens were cast to size ($\frac{1}{2}$ -in. dia.) in green-sand molds. His results are given in Table 2.

TABLE 2.—*Normal Sand-cast Aluminum-silicon Alloys (Daniels)*

Melt	Total Silicon	Ultimate Strength Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness	Specific Gravity
As sand-cast					
2063 ^a	0.14	11,050	29.2	20	2.68
2796	0.50	12,240	18.0	23	2.66
2798	0.64	12,270	12.8	24	2.67
2797	1.20	13,830	12.5	28	2.66
2794	2.80	16,370	10.2	31	2.64
2795	4.80	18,310	7.8	34	2.62
As quenched and aged ^b (1025—96 CW-300-8)					
2796		12,850	25.3	22	2.67
2798		13,690	19.7	24	2.67
2997		16,270	17.2	29	2.66
2794		18,160	13.8	30	2.64
2795		19,990	17.0	32	2.63
As annealed ^c (1025—96F)					
2796		11,630	26.0	19	2.67
2798		11,210	19.2	23	2.67
2797		11,120	19.5	21	2.68
2794		11,180	9.8	22	2.59
2795		10,800	6.0	22	2.62

^a Data from melt 2137, a remelt of melt 2063, and from melt 1660, of practically identical analysis.

^b 96 hr. at 552° C. (1025° F.), quenched in cold water, and aged 8 hr. at 149° C. (300° F.).

^c 96 hr. at 552° C. (1025° F.), and cooled over period of 7 days to room temperature.

⁴ U. S. Patent No. 1570893. Filed April 29, 1925; issued Jan. 26, 1926.

⁵ Samuel Daniels: Normal Sand-cast Alloys of Aluminum Containing Small Amounts of Silicon. *Jnl. Ind. & Eng. Chem.* (May, 1925) 485.

They confirm the possibility of improving elongation by prolonged heating and quenching, and of increasing hardness and strength by quenching as compared with slow cooling. It may be mentioned that the marked decreases in elongation on slow cooling as compared with quenching, in melts 2794 and 2795, are not in accord with the results of the work to be described in this paper, which showed the higher elongations after slow cooling. This cooling, however, was not nearly as slow as that employed by Daniels.

CONSTITUTION OF ALLOYS

Aluminum and silicon form a simple eutectiferous system whose constitution is discussed in detail in another contribution from the labora-

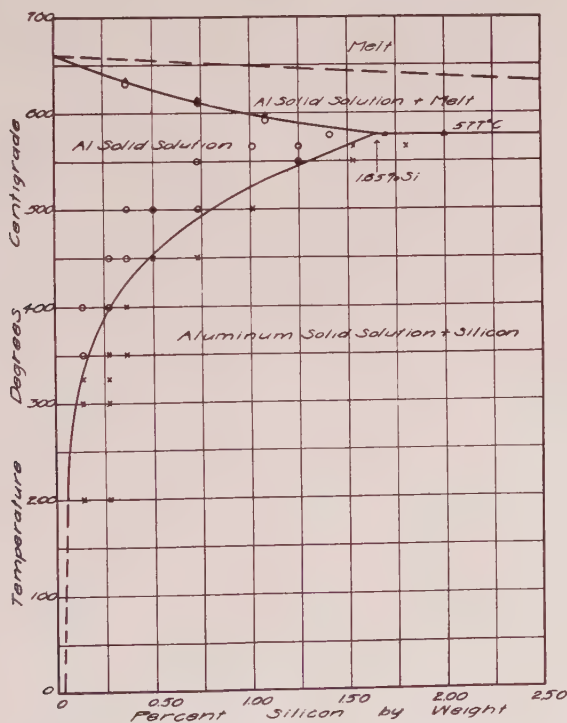


FIG. 1.—ALUMINUM END OF ALUMINUM-SILICON DIAGRAM (DIX AND HEATH).

ories of the Aluminum Co. of America.⁶ The diagram in Fig. 1 shows the constitution of alloys containing up to 2.5 per cent. silicon. Some of the more important data regarding the system, as given by Dix and Heath, may be noted:

⁶ E. H. Dix, Jr., and A. C. Heath: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. See page 164.

Melting point of pure aluminum.....	660° C. (1220° F.)
Eutectic composition.....	11.6 per cent. silicon
Eutectic temperature.....	577° C. (1071° F.)
Solubility of silicon in solid aluminum at 577° C.....	1.65 per cent.
Solubility of silicon in aluminum at room temperature	<0.05 per cent.

The solid solubility of silicon in aluminum and its variation with temperature are, of course, of great importance in the heat treatment of the alloys. It is interesting to note that one of the first serious investigators of this matter reported that the solubility of silicon in solid aluminum was substantially independent of temperature.⁷ This would preclude some of the heat-treatment effects that have been found to occur.

MODIFICATION OF ALLOYS

When aluminum-silicon alloys substantially free from certain special impurities are allowed to solidify slowly, as in sand molds, the silicon of the eutectic occurs in the form of rather large plates or rods. Alloys in this condition are said to be "normal." If such an alloy is caused to solidify with great rapidity, as by casting in a mold of high chilling power, it is found that the silicon occurs in very much smaller particles, which are more rounded in shape. This is apparently an undercooling effect.

The most striking results are obtained with alloys containing between 11.6 and about 14 per cent. silicon. These alloys are normally hyper-eutectic and on solidification contain primary silicon plus aluminum-silicon eutectic. After very rapid solidification it is found that the primary silicon has disappeared and that primary aluminum is present instead. At the same time the eutectic contains more than the normal amount of silicon and is greatly refined in structure. These changes seem to be due to the fact that the undercooling with respect to silicon is much more marked than that with respect to aluminum.

Similar effects can be obtained in sand castings by the addition to the molten metal of suitable amounts of certain agents which appear to obstruct the crystallization of the silicon much more effectively than that of the aluminum. The obstructing agent commonly employed is metallic sodium or some compound capable of producing sodium by reaction with molten aluminum. The amount of sodium necessary to produce the maximum refining effect in sand castings of ordinary size is only a few hundredths per cent. Aluminum-silicon alloys treated in such a way that the changed structure just described is obtained are said to be "modified," to distinguish them from the "normal" alloys mentioned above.

The transition from the normal to the modified condition is gradual rather than abrupt. Other conditions being the same, the addition of

⁷ D. Hanson and M. L. V. Gayler: The Constitution and Age-hardening of the Alloys of Aluminum with Magnesium and Silicon. *Jnl. Inst. Met.* (1921) **26**, 324.

increasing amounts of sodium to a normal alloy produces increasing refinement of structure and increasing strength and ductility up to a certain point, beyond which further additions of sodium produce less refinement and lower properties. The condition favorable to maximum strength is nearly but not exactly the same as that favorable to maximum elongation, and perhaps neither of these conditions is exactly that of maximum refinement of structure. In this work, the term "modified" refers to material in which the modification effect is approximately at its maximum, as judged by the attainment of substantially maximum elongation. Material in which the effect is less will be referred to as "partially modified," or as "undermodified" or "overmodified," as the sodium content is less or greater than that for maximum elongation.

Methods for the refining or modifying of aluminum-silicon alloys have been discussed elsewhere in detail, as has also the theory underlying the process.⁸

COMMERCIAL USE

The aluminum-silicon alloys are now widely used for castings. In this country, the alloy most commonly used for sand castings is that containing 5 per cent. silicon, usually in the normal condition. Smaller quantities of the 10 per cent. silicon alloy are used, also usually in the normal condition. The 13 per cent. silicon alloy, in the modified condition, is used to some extent in this country for sand castings and to a much greater extent in Germany. A 13 per cent. silicon alloy is also used in large quantities for die castings.

The aluminum-silicon alloys have been rolled into sheet and made into other wrought products. As yet, there is practically no commercial use of these alloys in the wrought condition, but there may well be such use in the future.

METHODS USED IN PRESENT INVESTIGATION

Table 3 shows the compositions by analysis of the alloys used in these investigations. The alloys containing 0.10 per cent. iron or less were made by adding metallic silicon to electrolytically refined aluminum at about 850° C. In all other cases, Hall-process aluminum was used and the silicon was introduced by means of an intermediate alloy.

Melting

All melting was done in plumbago crucibles in a Stewart oil-fired furnace. Usually 20-lb. heats were used, but some 10-lb. melts were made. The maximum melting temperatures were, approximately: 705° C. (1300° F.) for normal sand castings; 788° C. (1450° F.) for chill

⁸ R. S. Archer and L. W. Kempf: Modification and Properties of Sand-cast Aluminum-silicon Alloys. *Trans.* (1926) **73**, 581.

castings and for sand castings modified with metallic sodium; 955° C. (1750° F.) for sand castings modified with a salt flux.

TABLE 3.—*Compositions (by Analysis) of Aluminum Ingot and Alloys*

Sample Number	Copper, Per Cent.	Iron, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.
3444	0.02	0.07		14.02
3446	0.07	0.10		13.31
3448	0.18	0.51		12.86
3449	0.18	0.51		12.86
3454	0.18	0.51		12.86
3455	0.07	0.10		13.31
4127	trace	0.56	trace	0.33
4128	0.03	0.32		13.65
4305	0.03	0.08	nil	2.79
4431	0.02	0.07	nil	1.51
4911	0.07	0.24	nil	4.99
4948	0.23	0.32		13.60
4958	0.51	0.90		4.66
4967	0.23	0.32		12.60
4974	0.05	0.30		12.72
4974	0.03	0.46		5.01
4982	0.03	0.40		8.06
4983	0.03	0.34		11.06

Modification

Both the salt-flux and the metallic-sodium methods of modification were used. These have been described in the literature,⁹ and only a brief outline of the procedure will be given here.

The salt flux consists of two parts of sodium fluoride and one part of sodium chloride. A suitable amount of this flux (in these experiments, 2 per cent. of the weight of the charge to be treated) was spread over the surface of the molten alloy at about 940° C. (1724° F.) while the crucible was in the melting furnace. As soon as the flux had melted, the crucible was removed to the foundry floor and the flux was stirred into the metal with a carbon stirring rod. The charge then remained untouched until the pouring temperature was nearly reached, when the salt covering and dross were skimmed off. The pouring temperature in this case was 649° C. (1200° F.). Pouring took place approximately 18 min. after the addition of the flux.

The treatment with metallic sodium consisted in pouring the molten alloy at about 760° C. (1400° F.) on the requisite amount of metallic sodium placed in the bottom of a crucible preheated to a dull red heat. The melt was then returned to the hot furnace, with no flame on, and

⁹ R. S. Archer and L. W. Kempf: *Op. cit.*

allowed to stand for 15 to 20 min. before the castings were poured. When this method of modification was used, pouring took place between 662° and 689° C. (1225–1275° F.). The proper amount of sodium and the most favorable holding time were determined in previous experiments.¹⁰ When overmodified or undermodified test bars were desired they were poured before or after the period of time for proper modification had elapsed.

Test Specimens

The method of molding the sand-cast test bars is illustrated in Fig. 2. These bars have a test section $\frac{1}{2}$ in. in diameter with a gage length of 2 in. Chilled test bars of approximately the same dimensions were cast to size in a permanent mold made of cast iron. All cast bars were tested without machining.

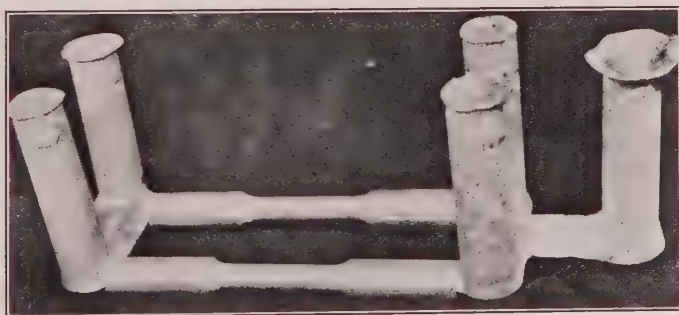


FIG. 2.—METHOD OF CASTING TEST BARS IN SAND.

Two of the alloys (samples 4305 and 4431) were cast into ingots approximately 3 in. square by 10 in. long, which were heated 18 hr. at 570° C., cooled slowly to 425° C., air-cooled to room temperature, reheated and forged to bar about $\frac{3}{4}$ in. square. Standard test bars 0.505-in. dia. with 2-in. gage length were machined from these forgings.

Testing

All tensile tests were carried out on a 10,000-lb. Olsen testing machine with self-aligning grips. Yield point was taken as the stress required to produce a total extension of 0.5 per cent. under load, using a Reihle extensometer reading to 0.0001 in. Brinell hardness measurements were made with an Alpha machine using a 10-mm. ball and a load of either 500 or 1000 kg., as indicated in the tables, applied for 30 seconds.

Heat-treating Methods

Most of the heat treatments were carried out in a Leeds & Northrup Homo furnace with special transformer equipment providing a wide

¹⁰ R. S. Archer and L. W. Kempf: *Op. cit.*

range of voltage changing by small steps, so that the energy input of the furnace could be very closely adjusted. As a result, the fluctuations in temperature in light loads properly placed in the furnace were within one degree Centigrade. The actual temperature measurements were made with base-metal thermocouples and a Leeds & Northrup potentiometer recorder having special ranges of temperature. This equipment was frequently checked at the freezing point of pure aluminum ($660^{\circ}\text{C}.$) and of the pure aluminum-copper eutectic ($548^{\circ}\text{C}.$) and at the boiling point of water. The temperatures given are believed to be accurate to within five degrees Centigrade at the higher temperatures and three degrees Centigrade at the lower temperatures. The precipitation heat treatments of very short duration at 250° , 300° and $400^{\circ}\text{C}.$ were carried out in a small niter pot heated in an electric furnace with automatic temperature control. The temperature measurements in these experiments are probably accurate to within five degrees Centigrade. The high-temperature or solution heat treatments were followed by either quenching or furnace cooling. The low-temperature or precipitation heat treatments were always followed by quenching. Quenching was done in water at room temperature.

Heat Treatment of Forgings

Table 4 shows the effect of certain heat treatments on the properties of two aluminum-silicon alloys in the forged condition. These alloys were made from electrolytically refined aluminum (99.95 per cent.). In one case the silicon content is slightly below the maximum solubility at the eutectic temperature, while in the other alloy the silicon content is

TABLE 4.—*Properties of Forged and Heat-treated Aluminum-silicon Alloys*

Sample Number ^a	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg.—10 Mm.	Treatment
	Lb. per Sq. In.				
4431	4,916	13,033	36.3	23.3	120 hr. @ 570° C. and furnace cooled to 170° C. in 40 hr.
4305	4,076	12,150	37.0	23.0	
4431	5,683	17,816	42.5	32.4	120 hr. @ 570° C., quenched and aged about 1 month at room temperature
4305	6,940	18,933	29.3	36.3	
4431	7,145	18,390	34.8	34.2	120 hr. @ 570° C., quenched and aged 100 hr. @ 150° C.
4305	8,020	19,925	31.0	38.0	

^a Sample 4431: silicon 1.51 per cent.; iron 0.07 per cent.; copper 0.02 per cent.

Sample 4305: silicon 2.79 per cent.; iron 0.08 per cent.; copper 0.03 per cent.

definitely above this limit. In order to obtain the maximum solution effect, these alloys were heated 120 hr. at $570^{\circ}\text{C}.$, which is just seven degrees Centigrade below the eutectic temperature. Microscopic exami-

nation of the material containing 1.51 per cent. silicon did not show any undissolved silicon. From this and previous experience it is considered that the time of heat treatment was ample to insure the attainment of maximum solution of silicon.



FIG. 3.—SAMPLE 4305; 2.79 PER CENT. SILICON. FORGING INGOT AFTER HEATING 18 HR. AT 570° C., COOLING SLOWLY TO 425° C. AND AIR-COOLING TO ROOM TEMPERATURE. UNETCHED. $\times 100$.

FIG. 4.—SAMPLE 4431; 1.51 PER CENT. SILICON; AS FORGED. UNETCHED. $\times 100$.

FIG. 5.—SAMPLE 4305; 2.79 PER CENT. SILICON. FORGED, HEATED 120 HR. AT 570° C. AND QUENCHED IN WATER. UNETCHED. $\times 100$.
(Reduced to $\frac{2}{3}$ original size.)

The results here given show a marked hardening effect due to quenching from 570° C. as compared with slow cooling.

Brinell hardness tests were made on specimens of these alloys in the quenched condition immediately after quenching and after aging one year

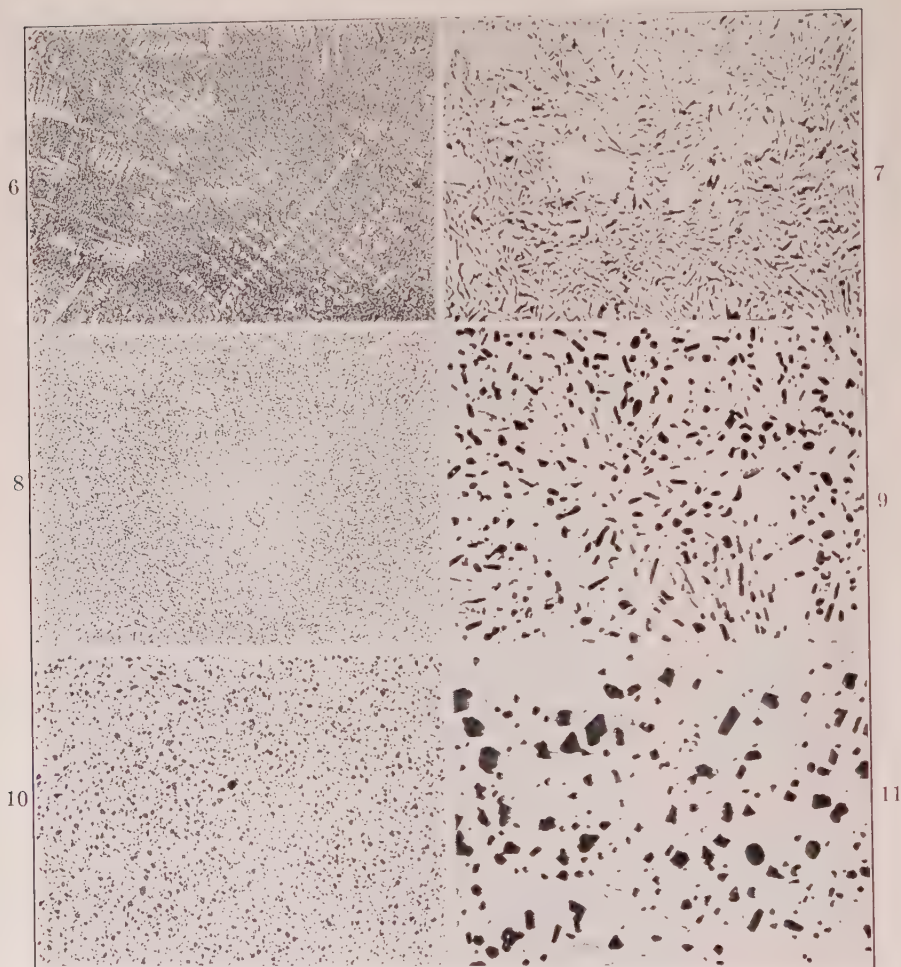


FIG. 6.—SAMPLE 4967; 12.6 PER CENT. SILICON; AS CAST IN PERMANENT MOLD. FIELD ABOUT HALFWAY FROM EDGE TO CENTER OF 0.5-IN. DIA. SECTION. UNETCHED. $\times 100$.

FIG. 7.—SAMPLE 4967; 12.6 PER CENT. SILICON; AS CAST IN PERMANENT MOLD. FIELD ABOUT HALFWAY FROM EDGE TO CENTER OF 0.5-IN. DIA. SECTION. UNETCHED. $\times 500$.

FIG. 8.—SAMPLE SHOWN IN FIG. 6 HEATED 1.5 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 100$.

FIG. 9.—SAMPLE SHOWN IN FIG. 6 HEATED 1.5 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 500$.

FIG. 10.—SAMPLE SHOWN IN FIG. 6 HEATED 40 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 100$.

FIG. 11.—SAMPLE SHOWN IN FIG. 6 HEATED 40 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 500$.

(Reduced to $\frac{2}{3}$ original size.)

at room temperature. Immediately after quenching, the hardness values obtained were 34.2 and 37.4 on samples 4431 and 4305 respectively. Corresponding values after one year were 34.45 and 37.6, showing substantially no change in hardness during the year. The aging treatment of 100 hr. at 150° C. was selected in light of some of the experiments carried out with particular reference to aging. These experiments will be described later. It will be noted from Table 4 that this aging treatment has produced slight increases in Brinell hardness and tensile strength and perhaps somewhat greater increases in yield point.

The effects of these heat treatments on elongation are not very conclusive, probably because of the rather large and variable grain size of the specimens.

The hardening effect of quenching from 570° C. clearly seems to be due to the retention in solid solution of a quantity of silicon greater than is retained during slow cooling.

The sample of higher silicon content (sample 4305) was apparently more completely softened by the annealing treatment than the other alloy. It seems plausible that the excess silicon assisted in the precipitation and agglomeration of the silicon from solid solution.

Fig. 3 shows the structure of one of the cast ingots after a preheating treatment prior to forging. Fig. 4 shows the structure of one of the alloys as forged. Fig. 5 shows the structure of the alloy containing 2.79 per cent. silicon after the solution heat treatment. In these and subsequent photomicrographs, the white constituent is aluminum or the aluminum-rich solid solution, while the dark constituent is silicon. The iron constituent appears in half-tone when present.

CHILL CASTINGS

Permanent-mold test bars were made of an alloy containing 12.6 per cent. silicon without the addition of any sodium. The effect of heating for a short and a long period of time at 565° C. and quenching is shown in Table 5. It will be noted that the elongation was markedly increased on quenching from this temperature. The tensile strength

TABLE 5.—*Effect of Heat Treatment on Physical Properties of a Chill Cast Aluminum-silicon Alloy*

Sample 4967: Copper, 0.23 Per Cent.; Iron, 0.32 Per Cent.; Silicon, 12.60 Per Cent.

Sample 4967: Copper, 0.25 Per Cent. Zinc, 100% Annealed				
Condition	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg. 10 Mm.
	Lb. per Sq. In.			
As cast.....	14,773	31,339	5.8	61.6
1.5 hr. @ 565° C., quenched.....	13,860	31,093	17.6	57.3
45 hr. @ 565° C., quenched.....	12,865	28,390	16.2	53.0

remains approximately the same as in the as-cast condition after a short heat treatment, and decreases after a long heat treatment. Microscopic examination (see Figs. 6 to 11) shows that there is progressive spheroidizing and particle growth of the silicon as the time of heat treatment is prolonged. This change in the form of the silicon particles is evidently the cause of the decreased hardness and increased plasticity.



FIG. 12.—SAMPLE 4911; ALLOY AS CAST IN SAND. NORMAL 4.99 PER CENT. SILICON. UNETCHED. $\times 100$.

FIG. 13.—SAMPLE SHOWN IN FIG. 12, HEATED 0.5 HR. AT 565° C. AND QUENCHED. UNETCHED. $\times 100$.

FIG. 14.—SAMPLE SHOWN IN FIG. 12 HEATED 20 HR. AT 565° C. AND QUENCHED. UNETCHED. $\times 100$.

FIG. 15.—SAMPLE SHOWN IN FIG. 12 HEATED 75 HR. AT 565° C. AND QUENCHED. UNETCHED. $\times 100$.

(Reduced to $\frac{2}{3}$ original size.)

NORMAL SAND CASTINGS

Most of the sand castings made of the unmodified aluminum-silicon alloys in this country contain about 5 per cent. silicon. The effect of heat treatment was investigated on two alloys of this type, one of fairly high purity, and the other containing larger amounts of iron and copper such as might be encountered in commercial practice.

Table 6 shows the effect of various heat treatments on the alloy of greater purity. It will be noted first that there is substantially no change in properties after aging 30 days at room temperature. Heating

for 30 min. at 565° C. and quenching produces a very appreciable increase in strength and hardness and a marked increase in elongation. As the time of heating at 565° C. is prolonged, the strength and hardness fall slightly, while the elongation increases. This is considered to be due to the change in the form of the silicon particles, which is illustrated in Figs. 12 to 15. Some of the bars heated 75 hr. were cooled in the furnace. The yield point, strength and hardness are much lower than in the bars that were quenched, while the elongation is distinctly higher. The increase in tensile strength produced by quenching as compared with slow cooling is 56 per cent. and the increase in Brinell hardness 53 per cent.

TABLE 6.—*Effect of Heat Treatment on the Physical Properties of a Normal Sand-cast Aluminum-silicon Alloy*

Sample 4911: Copper, 0.07 Per Cent.; Iron, 0.24 Per Cent.; Manganese, Nil; Silicon, 4.99 Per Cent.

Condition	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg. 10 Mm.
	Lb. per Sq. In.			
As cast.....		19,730	9.5	
As cast, 30 days at room temperature.....	7,857	19,430	9.5	37.1
Heated 30 min. @ 565° C., quenched.....		23,190	16.3	42.4
Heated 20 hr. @ 565° C., quenched.....		22,025	22.5	40.2
Heated 75 hr. @ 565° C., quenched.....	7,872	21,562	25.2	37.9
Heated 75 hr. @ 565° C., slowly cooled....	4,310	13,780	32.5	24.8
Heated 75 hr. @ 565° C., quenched, aged 28 days at room temperature.....	8,040	21,633	25.3	38.1
Aged 75 hr. @ 565° C., quenched, aged 100 hr. @ 150° C.....	9,700	21,550	20.2	40.4

Aging for 100 hr. at 150° C. produces distinct increases in yield point and hardness and a decrease in elongation, with substantially no change in tensile strength. The total increase in hardness from the slowly cooled to the artificially aged product is 63 per cent. Aging for 28 days at room temperature after the solution heat treatment has no appreciable effect.

Table 7 shows the effect of some heat treatments on a 5 per cent. silicon alloy of a lower degree of purity. It will be noted that the elongation is lower and the strength higher as cast. A 30-min. heat treatment at 565° C., which increased the elongation of the alloy of greater purity by 72 per cent., has scarcely affected the elongation of the less pure alloy. This is very likely due to the higher copper content of the latter. Heating for 40 hr., however, has produced a very marked increase in elongation, together with a slight but distinct increase in strength.

Modified Sand Castings

Sample 4128 is an alloy containing 13.65 per cent. silicon modified with metallic sodium. All of the test bars were poured at a time after the addition of sodium calculated to give approximately the highest obtainable elongation. The properties of this material as cast and after various heat treatments are given in Table 8.

It will be noted, first, that there is substantially no change in the properties of the cast bars on aging at room temperature up to 30 days.

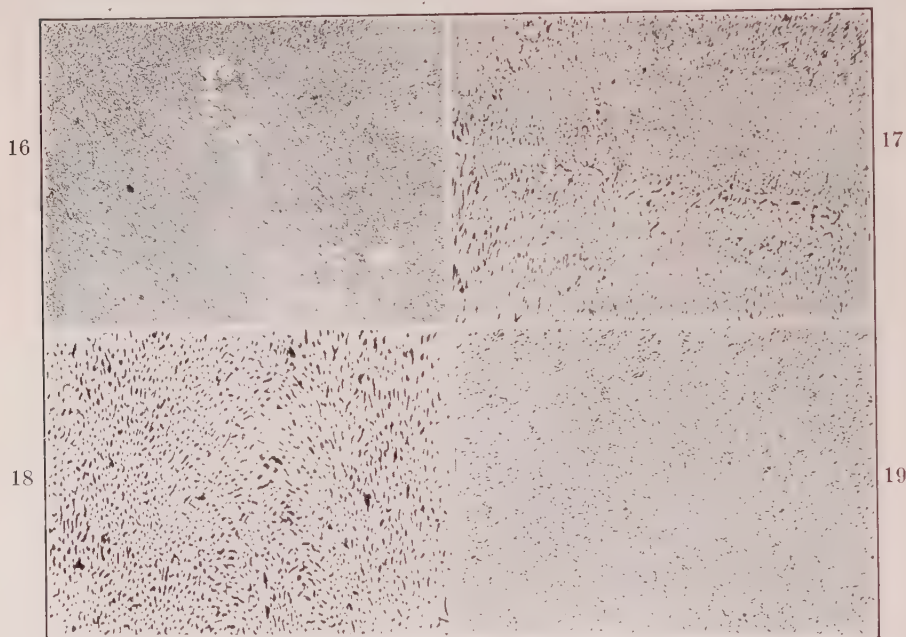


FIG. 16.—SAMPLE 4128; MODIFIED 13.6 PER CENT. SILICON ALLOY, AS CAST IN GREEN SAND. UNETCHED. $\times 100$.

FIG. 17.—SAME AS FIG. 16. $\times 500$.

FIG. 18.—SAME AS FIG. 16. $\times 1000$.

FIG. 19.—MATERIAL SHOWN IN FIG. 16 HEATED 0.5 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 100$.

(Reduced to $\frac{2}{3}$ original size.)

Heating for 30 min. at 565°C . and quenching has produced an increase in tensile strength of approximately 18.5 per cent. There is a slight increase in Brinell hardness and yield point. It is doubtful whether there is any definite change in elongation but such change as there is appears to be an increase. Prolongation of the time at 565°C . brings about definite decreases in yield point, strength and hardness, the final values on quenching after 75 hr. being lower than in the material as cast; the elongation appears to be slightly higher.

TABLE 7.—*Effect of Heat Treatment on the Physical Properties of a Normal Sand-cast Aluminum-silicon Alloy*

Sample 4958: Copper, 0.51 Per Cent.; Iron, 0.90 Per Cent.; Silicon, 4.66 Per Cent.

Condition	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg. 10 Mm.
	Lb. per Sq. In.			
As cast.....	9,080	19,414	4.25	45.6
Heated 30 min. @ 565° C., quenched.....	9,658	20,980	4.5	51.8
Heated 40 hr. @ 565° C., quenched.....	11,425	22,800	11.5	46.4

TABLE 8.—*Effect of Heat Treatment on the Physical Properties of a Modified Sand-cast Aluminum-silicon Alloy^a*

Sample 4128: Copper, 0.03 Per Cent.; Iron, 0.32 Per Cent.; Manganese, 0.02 Per Cent., Silicon, 13.65 Per Cent.

Condition	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 500 Kg. 10 Mm.
	Lb. per Sq. In.			
As cast, 2 hr. after casting.....		28,450	11.8	58.0
As cast, 20 hr. after casting.....		28,666	12.0	58.2
As cast, 30 days @ room temperature.....	13,027	28,510	12.5	57.9
30 min. @ 565° C., quenched.....	14,520	33,790	13.2	60.5
20 hr. @ 565° C., quenched.....		29,420	13.0	56.8
75 hr. @ 565° C., quenched, tested immediately	12,580	27,500	13.7	53.1
75 hr. @ 565° C., quenched, 100 hr. at 150° C.	13,570	25,600	13.0	51.2
75 hr. @ 565° C., quenched, 28 days at room temperature.....	11,455	27,683	13.5	53.4
75 hr. @ 565° C., slowly cooled.....	5,520	17,200	20.2	35.5

^a Values given are averages of three or more tests.

Aging for 28 days at room temperature seems to have practically no effect on the properties of the bars quenched after 75 hr. at 565° C. Aging for 100 hr. at 150° C. appears to have brought about slight decreases in tensile strength and hardness. This may represent an overaged condition. Slow cooling again results in markedly lower values for yield point, strength and hardness, and higher elongation.

Effect of Degree of Modification and of Silicon Content

The experiment just described was carried out with material intended to be modified to produce maximum elongation. In order to bring out the effects of heat treatment on undermodified and overmodified alloys and also the effect of silicon content, experiments were run on four alloys containing approximately 5, 8, 11 and 12.75 per cent. silicon refined to

various degrees ranging from normal to fully modified and cast in sand. The procedure consisted in pouring first one or two molds of normal alloy, then adding a suitable amount of sodium previously determined,¹⁰ and

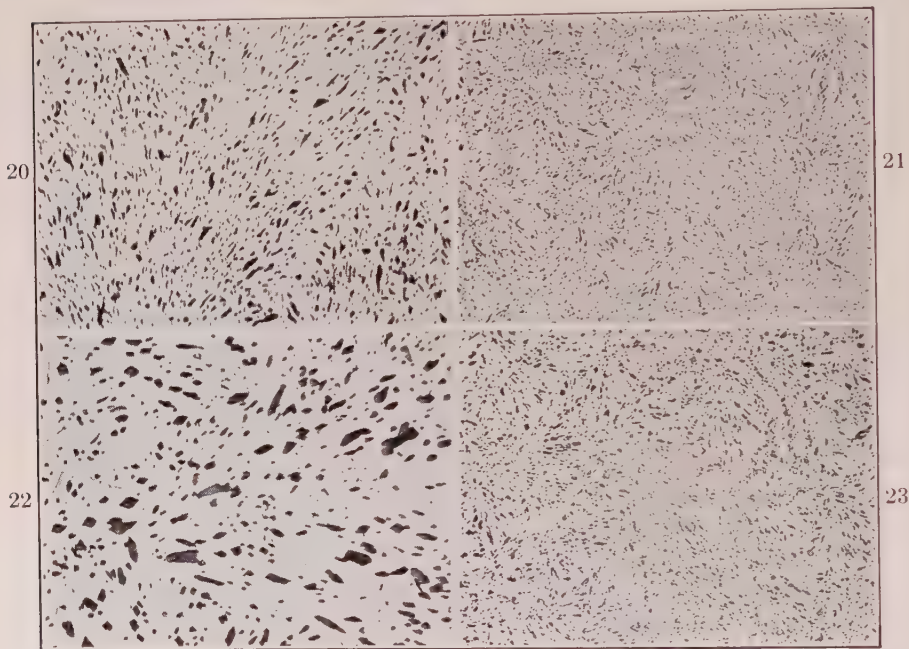


FIG. 20.—SAME AS FIG. 19. $\times 500$.

FIG. 21.—MATERIAL SHOWN IN FIG. 16 HEATED 20 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 100$.

FIG. 22.—SAME AS FIG. 21. $\times 500$.

FIG. 23.—MATERIAL SHOWN IN FIG. 16 HEATED 75 HR. AT 565°C . AND QUENCHED. UNETCHED. $\times 100$.

(Reduced to $\frac{2}{3}$ original size.)

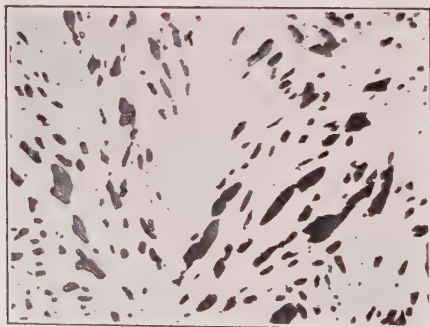


FIG. 24.—SAME AS FIG. 23. $\times 500$.
(Reduced to $\frac{2}{3}$ original size.)

¹⁰ R. S. Archer and L. W. Kempf: *Op. cit*

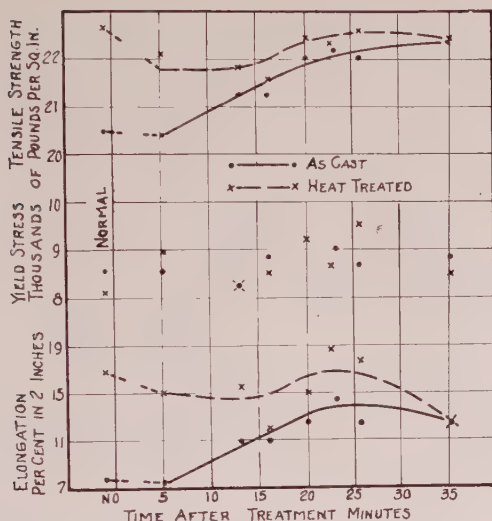


FIG. 25.—EFFECT OF HEAT TREATMENT (40 HR. AT 565° C.-QUENCH) AND DEGREE OF MODIFICATION, AS INDICATED BY TIME AFTER TREATMENT WITH SODIUM, ON SAND-CAST ALLOY. SAMPLE 4975; SILICON, 5.01 PER CENT.

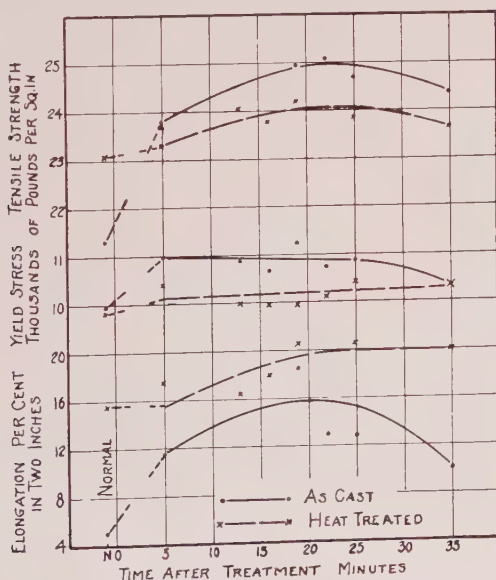


FIG. 26.—EFFECT OF HEAT TREATMENT (40 HR. AT 565° C.-QUENCH) AND DEGREE OF MODIFICATION, AS INDICATED BY TIME AFTER TREATMENT WITH SODIUM, ON SAND-CAST ALLOY. SAMPLE 4982; SILICON, 8.06 PER CENT.

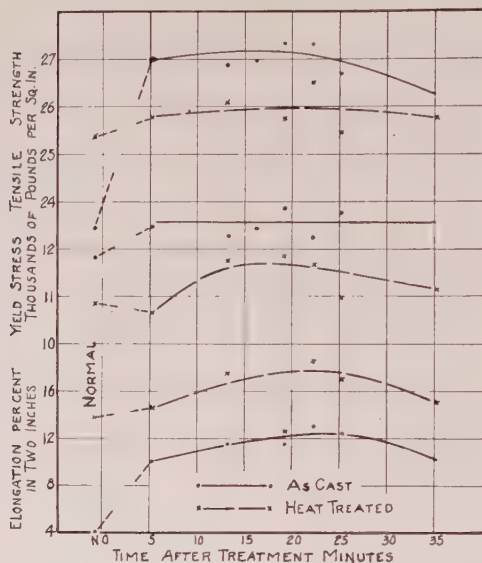


FIG. 27.—EFFECT OF HEAT TREATMENT (40 HR. AT 565° C.-QUENCH) AND DEGREE OF MODIFICATION, AS INDICATED BY TIME AFTER TREATMENT WITH SODIUM, ON SAND-CAST ALLOY. SAMPLE 4983; SILICON, 11.06 PER CENT.

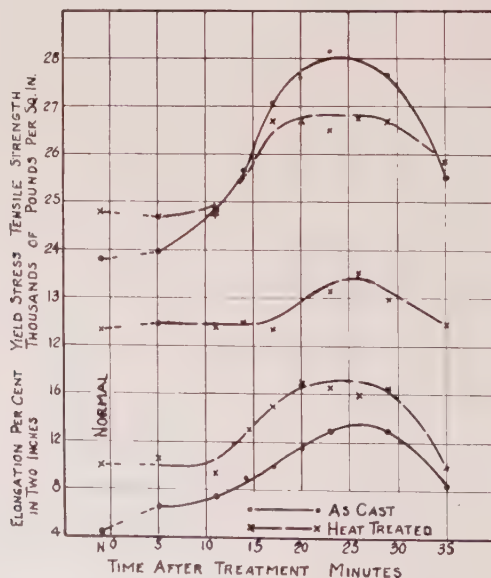


FIG. 28.—EFFECT OF HEAT TREATMENT (40 HR. AT 565° C.-QUENCH) AND DEGREE OF MODIFICATION, AS INDICATED BY TIME AFTER TREATMENT WITH SODIUM, ON SAND-CAST ALLOY. SAMPLE 4974; SILICON, 12.72 PER CENT.

pouring test-bar molds at various intervals up to and beyond the period considered favorable for the attainment of maximum elongation. One bar of each mold was tested as cast, while the duplicate bars were heated 40 hr. at 565° C. and quenched. The results are given in the curves of Figs. 25 to 28. It is to be noted that each point plotted represents only one test bar.

In Fig. 25, referring to the 5 per cent. silicon alloy, it is seen that the maximum effects of this heat treatment on both strength and elongation occur in the normal material. Both strength and elongation are markedly increased. The minimum effects of heat treatment seem to occur in material slightly undermodified. The changes in yield point are so slight and indefinite that no curves have been drawn.

In Fig. 26, referring to the 8 per cent. silicon alloy, the maximum effects on tensile strength and elongation are again found in the normal material, the values for both of these properties being increased. It is interesting to note that after the addition of sodium the effect of this heat treatment on the tensile strength is reversed, the strength of the heat-treated bars being lower than that of the corresponding bars as cast. The elongation is in all cases higher.

A similar reversal in the effect of heat treatment on tensile strength is seen in Fig. 27, referring to the 11 per cent. silicon alloy. The strength of the normal bars is increased, while that of the modified bars is decreased. Elongations are in all cases markedly increased.

In Fig. 28, showing the results on the 12.7 per cent. silicon alloy, the strength effect is again reversed, but this time only at certain degrees of modification. The strengths of the normal and of the overmodified and undermodified bars are increased, while those of the well modified bars are decreased. Elongations are in all cases increased, but the effect varies with the degree of modification. The yield points of the bars in the as-cast condition were not determined.

SUMMARY ON NORMAL AND MODIFIED ALLOYS

The curves plotted in Fig. 29 summarize the results of prolonged heat treatment (40 hr.) at 565° C. followed by quenching on normal and modified alloys of various silicon contents cast in sand. The following generalizations can be made regarding the effects of this particular heat treatment: (1) The tensile strengths of the normal alloys are increased. (2) The tensile strengths of the modified alloys are decreased, especially at intermediate silicon contents. At 5 and at 13.65 per cent. silicon there is little change in the tensile strength. (3) Elongation is increased by heat treatment in both the normal and modified alloys until the compositions of the normal and modified eutectics are approached. Little, if any, increase in elongation occurs in the modified bars containing 13.65 per cent. silicon. The curve for the normal bars indicates that

there would be little improvement in elongation with silicon contents above that of the normal eutectic.

HARDENING BY QUENCHING DURING INITIAL COOLING OF CASTINGS

It was discovered by one of the authors¹¹ that a marked heat treatment effect can be produced by quenching modified sand-cast aluminum-silicon alloys shortly after solidification; that is, during the initial cooling of the casting. Some of the experimental work is described below.

In each of the experiments eight test-bar molds were poured. Approximately 40 to 50 sec. were required to pour these molds. During this time some sodium might have burned out, and the temperature of the

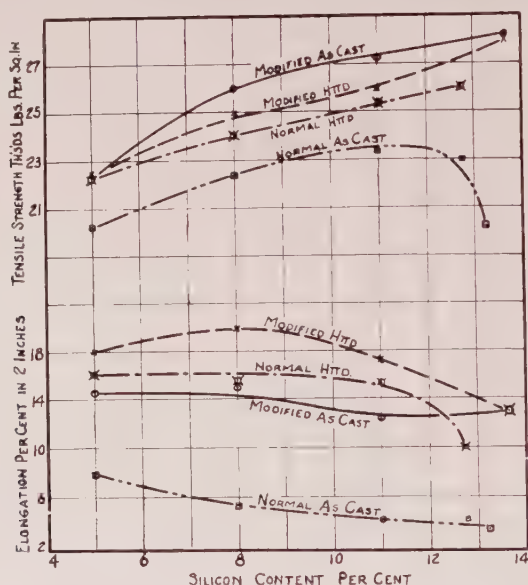


FIG. 29.—EFFECT OF HEATING 40 HR. AT 565° C. AND QUENCHING ON NORMAL AND MODIFIED SAND CASTINGS CONTAINING 5 TO 13.6 PER CENT. SILICON.

metal might have dropped slightly. This gradual change in sodium content or pouring temperature might produce changes in physical properties which would be confused with the effects of the principal factor under consideration; that is, the time between pouring and quenching. To prevent any confusion from this source, the molds were quenched in water in the following order: 1, 8, 2, 7, 3, 6, 4 and 5.

In one of the experiments on a modified alloy, a No. 18 gage chromel-alumel thermocouple was cast in the center of the test section of a test bar in one mold, to obtain a cooling curve from which the quenching temperatures could be approximated.

¹¹ Douglas B. Hobbs: U. S. Patent No. 1570893. Filed April 29, 1925. Issued Jan. 26, 1926.

In Fig. 30 the rate of cooling of this test bar is shown in the lower curve, while the upper curves show the tensile properties obtained in two of the experiments. Sample 3448 contains 12.86 per cent. silicon, 0.51 per cent. iron, and 0.18 per cent. copper. Sample 3444 is an alloy of high purity containing 14.02 per cent. silicon, 0.07 per cent. iron, and 0.02 per cent. copper. Both of these alloys were modified with salt

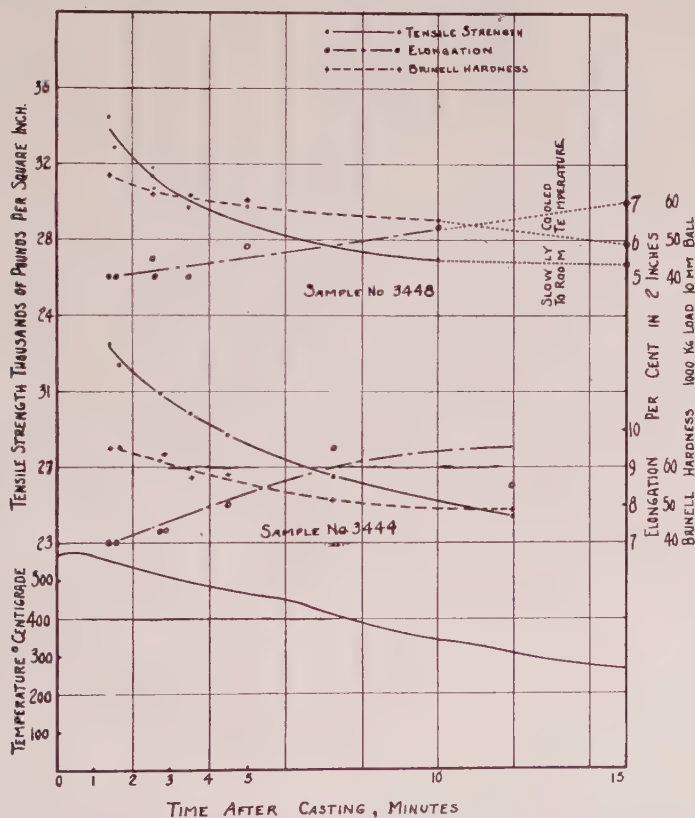


FIG. 30.—EFFECT OF QUENCHING AT VARIOUS PERIODS AFTER POURING ON MODIFIED SAND-CAST ALLOYS. SAMPLE No. 3448; SILICON, 12.86 PER CENT.; IRON, 0.51 PER CENT.; COPPER, 0.18 PER CENT. SAMPLE No. 3444; SILICON, 14.02 PER CENT.; IRON, 0.07 PER CENT.; COPPER, 0.02 PER CENT.

flux. The test-bar castings were taken from the sand and quenched in water at various intervals after pouring, as shown in the diagram. It is seen that the strength and hardness decrease continuously as the time between pouring and quenching increases up to perhaps 10 min. after pouring. At the same time the elongation increases.

In sample 3446, a modified 13 per cent. silicon alloy of high purity (Table 9), the intervals before quenching were concentrated within the

TABLE 9.—*Effect of Quenching during Initial Cooling of Modified Sand Castings*

Sample 3446: Silicon, 13.31 Per Cent.; Iron, 0.10 Per Cent.; Copper, 0.07 Per Cent.

Mold No.	Time between Casting and Quenching, Min.	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 1000 Kg. 10 Mm. Ball
		Lb. per Sq. In.			
7	1.50	15,085	34,150	8.3	67
1	1.75	16,495	33,125	8.0	66
6	2.10	16,240	33,060	12.5	64
2	2.30	15,465	32,625	11.8	64
3	2.65	15,215	32,070	13.3	64
5	2.73	14,960	32,125	14.3	65
4	Cooled slowly to room temperature	11,825	24,885	18.3	49
8 ^a	Cooled slowly to room temperature	12,675	25,130	18.0	50

^a Only one bar was tested. The physical properties in all other cases are the average of two bars.

TABLE 10.—*Effect of Quenching during Initial Cooling of Modified Sand Castings*

Sample 3449: Silicon, 12.86 Per Cent.; Iron, 0.51 Per Cent.; Copper, 0.18 Per Cent.

Mold No.	Time between Casting and Quenching, Min.	Yield Point	Tensile Strength	Elongation in 2 In., Per Cent.	Brinell Hardness 1000 Kg. 10 Mm. Ball
		Lb. per Sq. In.			
8	1.23	18,138	36,775	6.5	72
1	1.55	17,760	33,885	5.0	68
7	2.00	16,138	33,450	5.5	66
2	2.20	16,100	33,640	5.0	69
6	2.62	16,640	33,950	6.5	65
3	2.72	16,125	31,915	5.0	62
4	3.38	15,700	32,150	5.5	64
5	Cooled slowly to room temperature	13,150	28,100	7.5	54

The above results are an average of two bars.

first 3 min. after pouring. One casting was allowed to remain in the mold until room temperature had been reached.

Table 10 shows the results on a modified 13 per cent. silicon alloy of commercial grade in an experiment in which the intervals between pouring and quenching were concentrated within 4 min. One mold was again cooled slowly to room temperature. The strength changes are similar to those previously shown. The changes in elongation are

TABLE 11.—*Effect of Quenching during Initial Cooling of Normal Sand Castings*

Sample 3455: Silicon, 13.31 Per Cent.; Iron, 0.10 Per Cent.; Copper, 0.07 Per Cent.

Mold No.	Time between Casting and Quenching, Min.	Tensile Strength Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness 1000 Kg. 10 Mm. Ball
8	1.82	21,035	2.3	59
1	2.08	21,060	2.3	59
2	4.03	19,940	2.3	53
7	5.42	19,830	2.3	50
3	8.02	19,665	3.0	48
6	9.95	19,370	2.5	46
4	12.00	18,440	3.0	45
5	Cooled slowly to room temperature	19,530	3.5	47

The above results are the average of two bars.

TABLE 12.—*Effect of Quenching during Initial Cooling of Normal Sand Castings*

Sample 3454: Silicon, 12.86 Per Cent.; Iron, 0.51 Per Cent.; Copper, 0.18 Per Cent.

Mold No.	Time between Casting and Quenching, Min.	Tensile Strength Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Brinell Hardness 1000 Kg. 10 Mm. Ball
1	2.33	20,875	1.5	65
8	3.93	18,980	1.5	50
2	6.30	19,875	1.5	57
7	7.72	19,795	1.5	55
3	9.97	19,975	1.5	61
6	11.98	18,800	1.5	50
4	13.97	17,800	1.5	54
5	Cooled slowly to room temperature	18,075	1.5	53

The above results are the average of two bars.

not as striking as in the results given in Table 9, but are in the same direction.

The effects of quenching during the initial cooling on normal sand castings, containing approximately 13 per cent. silicon, are shown in Tables 11 and 12. The results are, in general, of the same nature as in the modified alloys, but the changes are less marked.

Microscopic examination of one of the modified bars quenched 1.5 min. after pouring showed that it had not solidified completely. The lower right-hand portion of the field in Fig. 31 represents material molten at the time of quenching, while the upper left-hand portion shows the structure of the outer part of the test bar which had already solidified. The very rapid chilling of the core has produced a higher degree of dis-

persion of the silicon than has been observed in any ordinary modified sand casting. This specimen was taken near the shoulder of the test bar. Another specimen taken about halfway between the shoulders of the same bar showed still higher dispersion of the silicon. It was noted, in the case of unmodified test bars, that if quenching was carried out within about 2.3 min. after pouring, the risers were quite soft and broke in handling, whereas in the case of modified bars it was possible to quench 1.5 min. after pouring without breaking.

In view of the fact that modified sand castings can be materially hardened by a short heat treatment at 565°C. , followed by rapid cooling, it appears that the increase in yield point, tensile strength and Brinell



FIG. 31.—SAMPLE 3446; MODIFIED 13.31 PER CENT. SILICON ALLOY, CAST IN GREEN SAND, REMOVED FROM MOLD AND QUENCHED 1.5 MIN. AFTER POURING. ETCHED IN 3 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 1000$.

(Reduced to $\frac{2}{3}$ original size.)

hardness that results from quenching directly from the mold is due largely to the retention of silicon in solid solution. An additional factor, which may be to some extent responsible, is the prevention of some particle growth or spheroidizing that might have taken place if the casting were allowed to cool without interruption in the mold, or even if it were allowed to cool slowly on the foundry floor.

PRECIPITATION HARDENING

From the marked decrease in the solubility of silicon in aluminum with decreasing temperature, and the great hardness of silicon as compared with aluminum, it would seem possible to produce considerable hardening by either natural or artificial aging, following a solution heat treatment. The absence of any appreciable aging effect at room temperature had been noted in many instances. Experiments were under-

taken to determine the possibilities of age-hardening at elevated temperatures. The two forged alloys, samples 4431 and 4305, containing 1.51 and 2.79 per cent. silicon were heated 72 hr. at 570° C., quenched in water and reheated at various temperatures for various periods of time. All samples were quenched in water after the reheating treatments.

The results on the 2.79 per cent. silicon alloy are shown in Fig. 32. It is seen that at each temperature the hardness rises to a maximum and then decreases. The amount of the hardness increase is not very great

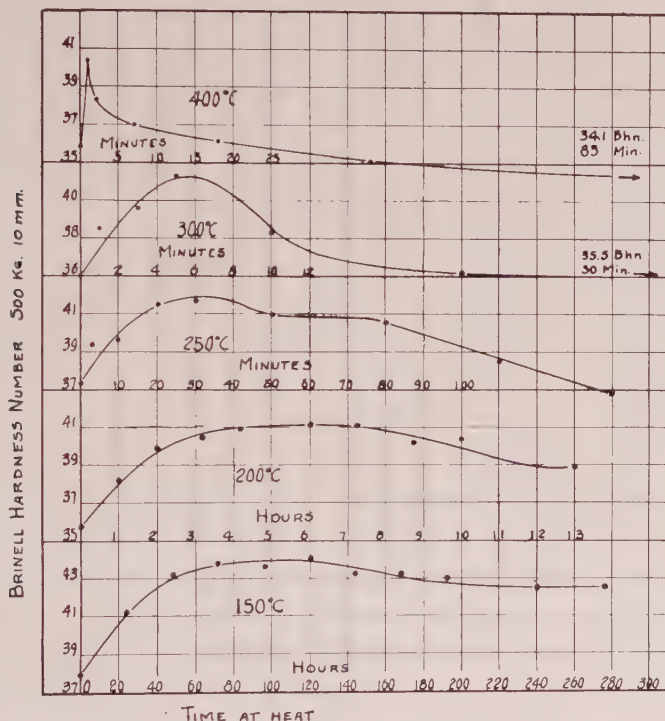


FIG. 32.—EFFECT OF REHEATING AT VARIOUS TEMPERATURES ON BRINELL HARDNESS OF FORGED 2.79 PER CENT. SILICON ALLOY, HEATED 72 HR. AT 570° C. AND QUENCHED.

at any temperature, and is not much greater at the low temperatures than at the high temperatures. The time required to attain maximum hardness, of course, lessens as the temperature of reheating is increased. This is shown in Fig. 33, in which the time required to attain maximum hardness is plotted on a logarithmic scale against the aging temperature on an arithmetical scale. The result is a straight line.

It was thought that perhaps the failure to obtain a greater increase in hardness in these treatments was due to the effect of the undissolved silicon particles which might act as nuclei and prevent the development of a fine dispersoid. Aging treatments were therefore carried out at

150° and 200° C. for various periods of time on the alloy containing only 1.51 per cent. silicon, in which no undissolved silicon could be seen after the solution heat treatment. The results are given in Table 13, from which it will be seen that the increase in hardness is of the same order as that obtained in the 2.79 per cent. silicon alloy.

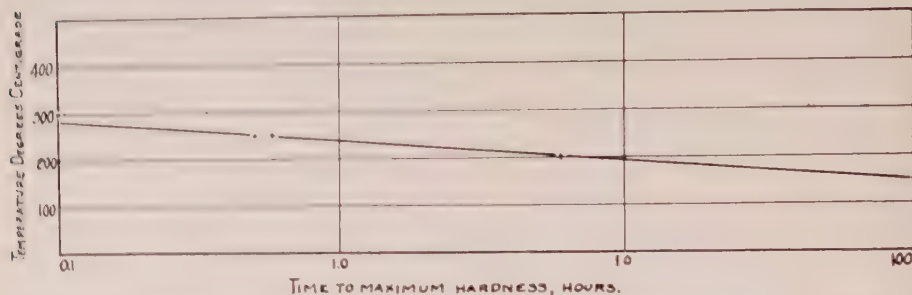


Fig. 33. —Effect of reheating temperature on time required to produce maximum hardness in quenched aluminum-silicon alloy.

There has not yet been opportunity to inquire sufficiently into the causes of this rather interesting absence of marked age-hardening. One specimen containing 1.51 per cent. silicon, heated 120 hr. at 570° C., quenched and reheated at various temperatures, was examined microscopically for evidence of precipitated silicon. A very fine precipitate



Fig. 34.

Fig. 35.

Fig. 34. —SAMPLE 4431; 1.5 PER CENT. SILICON ALLOY. FORGED, HEATED 120 HR. AT 570° C., QUENCHED AND REHEATED 40 HR. AT 400° C. ETCHED IN 1 PER CENT. HF. X 500.

Fig. 35. —SAME AS FIG. 34. X 1000.
(Reduced to $\frac{2}{3}$ original size.)

could be definitely seen after reheating at 300° C. This precipitate was more easily observed after heating 40 hr. at 400° C., in which condition it is shown in Figs. 34 and 35. It seems that the area occupied by silicon in these photomicrographs is larger than would be expected from the silicon content of the alloy. It was also noted that the silicon particles

did not polish out in relief to as great an extent as in some other specimens; such as that shown in Fig. 5, for example. There has not been enough work done on this phase of the subject to say whether these observations have any significance. The dispersion of the silicon seems to be general, except for a slight concentration along the grain boundaries, as would be expected.

TABLE 13.—*Precipitation Hardening of an Aluminum-silicon Alloy*
Forged Bars Containing 1.51 Per Cent. Silicon; 0.07 Per Cent. Iron; 0.02 Per Cent. Copper (Sample 4431) Were Heated 72 Hr. at 570° C., Quenched in Water, and Reheated to Temperatures Indicated, and Quenched

150° C.		200° C.	
TIME, HR.	BRINELL HARDNESS 500 KG., 10 MM.	TIME, HR.	BRINELL HARDNESS 500 KG., 10 MM.
0	34.4	0	32.3
1	34.45	1	35.2
2.3	35.75	2	37.5
3.6	35.65	3.16	37.8
5.0	35.5	4.16	37.8
25.0	37.35	6.0	38.9
49	38.45	7.25	38.8
73	39.4	8.75	38.5
97	38.85	10.0	38.3
121	39.85	13.0	37.7
145	39.35		
169	37.85		
193	37.85		
217	38.2		
241	38.2		
265	38.4		
289	38.0		

PRACTICAL CONSIDERATIONS

These results suggest that it may be well worth while to heat-treat aluminum-silicon alloy castings in commercial practice. The maximum strength attained is below that attainable in other heat-treated alloys, such as those of aluminum with copper, but the elongation and plasticity are high. The tensile properties are to be considered together with the other characteristic properties of the aluminum-silicon alloys, among which may be mentioned: good casting qualities—fluidity, freedom from hot shortness, and freedom from leaks; excellent resistance to corrosion; low thermal expansivity; high electrical and thermal conductivity; low specific gravity; rather poor machinability; low elastic limit and low endurance limit (before heat treating). Heat treatment may improve

some properties that were not determined in the work described, such as resistance to corrosion and endurance limit.

It should be noted that the work described is exploratory in character and is not, in the authors' opinion, sufficiently complete to make possible reliable conclusions regarding the properties that could be realized on a commercial scale. Account should be taken of commercial variations in alloy composition and casting practice. Furthermore, it would probably be impractical to employ on a large scale heat-treating temperatures as close to the melting point of the aluminum-silicon eutectic as were employed in this work. It would be desirable, therefore, to determine the effect of lower temperatures.

A consideration of some importance concerns the relative ease of heat treating as compared with modifying. The best product that can be made by a given process is of little interest unless it can be made with a rather high degree of consistency. It has been found in one commercial foundry that the heat treatment of aluminum-copper alloy castings can be controlled more easily than the modification of aluminum-silicon alloys. It cannot, of course, be said that this experience would be universal, or that the heat treatment of aluminum-silicon alloy castings would produce more consistent results than modification.

DISCUSSION AND SUMMARY

The heat treatment effects in aluminum-silicon alloys may be considered as due to one or more of these structural changes: solution; precipitation; spheroidizing; grain growth.

Solution.—Strength and hardness may be increased very materially, in some cases by well over 50 per cent., by quenching from about 565° C. as compared with cooling slowly. This hardening is accompanied by decreased plasticity and usually by decreased elongation. From the known constitution of the system, it is to be expected that the magnitude of the solution effect will vary with the quenching temperature up to the melting point of the eutectic (577° C.), increasing as the temperature is increased.

Results analogous to those of a solution heat treatment can be produced by quenching castings shortly after solidification.

Precipitation. Aging at room temperature has substantially no effect on the tensile properties or hardness of aluminum-silicon alloys, either as cast or after a solution heat treatment. Aging at elevated temperatures (150°–400° C.) after a solution heat treatment at 570° C. may increase hardness by about 15 to 20 per cent. This hardening seems to be accompanied by decreased plasticity and, usually, ductility.

Spheroidizing.—Spheroidizing and growth of the silicon particles are very marked on heating at about 565° C., but also occur at lower tem-

peratures. They result in decreased hardness and strength and increased plasticity, usually with increased ductility. These effects increase with the temperature and time of heat treatment.

Grain Growth.—Grain growth is to be expected in wrought aluminum-silicon alloys when they are heated above the temperature of recrystallization. This phase of the subject was not investigated in the work here described.

Conclusions.—In general, treatment for a short time at temperatures around 565° C., followed by quenching, favors the predominance of the solution effect, while a long-time treatment favors the predominance of the spheroidizing effect. Thus the strength and hardness of castings may be increased by short heat treatments but reduced by long heat treatments. The plasticity of a cast alloy is apt to be decreased by a short treatment, due to the solution effect, but is increased as the time of treatment is prolonged, due to the spheroidizing effect. Elongation is a complex property depending on both strength and plasticity. It may be increased by a solution heat treatment which at the same times decreases plasticity. It may be further increased when the spheroidizing effect increases plasticity, and might ultimately be decreased by the loss of strength due to spheroidizing, although this stage was not reached in the experimental work here covered.

DISCUSSION

S. L. HOYT, Schenectady, N. Y.—It would seem that much of this work could be very well done by the college laboratories, but instead of the colleges supplying material of this kind to the industries for their utilization we find the industries supplying teaching material to the colleges.

P. D. MERICA, New York, N. Y.—I noticed the difference in structure caused by a high temperature anneal followed by a draw, in the sense of spheroidizing the silicon particles. I do not notice any reference in the paper to the effect that that change of structure will have on the machining, but I think it must have a very important one. I would be interested to know what that effect is.

R. S. ARCHER.—There is considerable reason to think that change in particle shape should have a marked effect on machining qualities, but there is not sufficient experience on any scale to tell with certainty what the effect is.

The principal difficulty in machining the ordinary aluminum silicon alloys, by which I mean alloys containing 13 per cent. or less of silicon, is due to the softness of the material which causes dragging and building up of aluminum on the tool edge and similar effects. With higher silicon content, especially with primary silicon present, an abrasive effect on the tool becomes apparent. It would be expected that the spheroidizing of the silicon particles by heat treatment would diminish the abrasion by making them smoother and by decreasing the probability of fracture with production of sharp edges. On the other hand, the increase in plasticity by heat treatment might be expected to increase the tendency of the alloys to drag so that the net results do not appear very certain and really would have to be determined by extended machining tests.

Condition of Thorium in Thoriated Tungsten Filament

BY ANCEL ST. JOHN, PH.D., NEW YORK, N. Y.

(Detroit Meeting, September, 1927)

AT THE New York meeting of the Institute of Metals Division in February, 1927, Jeffries and Tarasov presented a paper on Tungsten and Thoria,¹ in which the experimental facts were interpreted in accordance with the prevailing point of view that the thorium is present as the oxide, thoria.

In discussing that paper the writer of this article stated that his own investigations, which had been unavailable to Messrs. Jeffries and Tarasov, showed that the so-called "thoriated" tungsten filament failed to disclose any sign of the oxide when subjected to X-ray diffraction analysis, but did give plenty of evidence of the presence of metallic thorium and, in certain cases, of a material believed to be an alloy of tungsten in thorium. Since these results were completely at variance with the results reported in the paper under discussion and with other papers which had preceded it from time to time in the past, it was felt that further discussion should be withheld until the new evidence could be presented adequately. Arrangements were therefore made to present that evidence at this meeting.

MATERIAL EXAMINED

The material examined was high-emission filament such as is used in radio tubes, supposed to contain about 0.75 per cent. thoria. The actual analysis was not stated.

SCOPE OF THE INVESTIGATION

The investigation was undertaken because of a feeling that the thorium present in filamentary material of this type exists as metallic thorium or as an alloy of thorium and tungsten and not as the oxide. Attention was therefore directed to determining:

1. The minimum amount of thoria detectible in a mechanical mixture of thoria powder and finely divided tungsten.
2. The amount of thoria detectible in the filament.
3. The condition of any thorium present in other form than as thoria.
4. The amount of thorium dissolved in the tungsten.

¹ *Proc. Inst. Metals Div., A. I. M. E. (1927)* 395.

In the course of the investigation more than 100 exposures were made, most of which were direct comparisons of the patterns of two samples. Fifty-eight exposures were made on the filament. Of these 10 showed unmistakably lines attributable only to thorium, or to a component hitherto unknown, which showed a characteristic structure and gave a characteristic pattern; 12 showed clear indications of such lines, and eight showed suggestions of them. Six of the 58 exposures were made to bring out the extent of the thoria content, three were made in a special manner to determine the extent of solution of thorium in tungsten, and the remainder were failures resulting from experi-

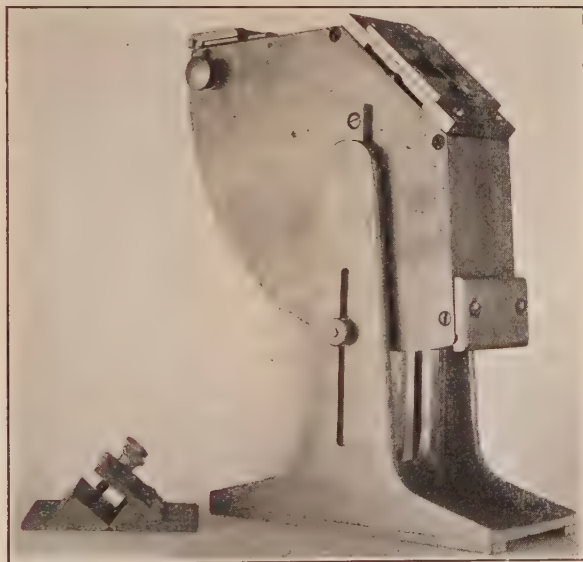


FIG. 1.—ST. JOHN X-RAY DIFFRACTOMETER, 1926 MODEL.

mental difficulties. In all cases where the experimental procedure was suitable for the detection of very small amounts of thorium or the new component, lines attributable only to one or the other were present. In a few cases such lines were observed to have surprising intensity when the experimental conditions were not favorable, suggesting the segregation of the corresponding constituent. No signs of the pattern of thoria were found, even under the most favorable conditions. The amount of thorium dissolved in the tungsten was found to be inappreciable.

METHODS USED

The diffractometers used were of the type originally designed by the writer for the Union Carbide and Carbon Research Laboratories. A more recent instrument of this type is illustrated in Fig. 1. It is provided

with interchangeable specimen holders for the surface reflection method with materials highly opaque to X-rays, for the powder method as usually practised and for the writer's precision method with transmitted radiation. All of these methods were used in the course of the investigation. The X-rays were derived from the usual type of Coolidge tube with water-cooled molybdenum target operated at 30,000 volts and 25 milliamperes. Exposures ranged from 16 to 72 hr. Zirconia filters were used at times and omitted at others.

IS THORIA PRESENT IN THE FILAMENT?

As already stated, no signs of the pattern of thoria were found even under the most favorable circumstances. Two prominent lines of the thoria pattern lie between two of the lines of the tungsten pattern, but far enough removed to be clearly distinguishable even when very faint. Taking advantage of this, specimens about $\frac{3}{4}$ -in. square were mounted at the proper angle to focus sharply in this region by surface reflection. Under these circumstances there should be enough particles of the minor constituent favorably placed for diffraction to give a recognizable line for concentrations under 1 per cent. In tests of mechanical mixtures of very finely divided tungsten powder and powdered thoria, it was found that the thoria lines could be faintly detected for mixtures containing 0.2 per cent. In similar tests on a large number of strands of filament side by side on a card, no signs of the lines could be discovered. It must be concluded therefore that the amount of thoria present is less than 0.2 per cent. or that it is in such a state of submicroscopic subdivision as to give a weaker pattern than the material used as control.

IS METALLIC THORIUM PRESENT IN THE FILAMENT?

The direct comparison of a single strand of the filament with a thin compressed specimen of powdered thoria mounted for the transmission method is illustrated in Fig. 2. In the writer's variation of the transmission method, the face of the slit system is at 45° to the X-ray beam and the upper edge of the slit is on the axis of the instrument. The specimen is placed against the slit system on the tube side, so that a portion is in contact with this edge of the slit and hence is on the axis. As a result the lines are sharply defined over the entire range of the instrument. In Fig. 2 there is no sign in the pattern of the filament, on the left, of any of the strong lines of the thoria pattern. On the other hand, there is a distinct break in the pattern of the filament about $\frac{1}{4}$ in. from the right-hand edge, the left-hand portion being the pattern of tungsten plus the pattern of thorium, and the right-hand portion the pattern of a material having the same face-centered cubic structure as thorium but with the atoms somewhat closer together. The side of the unit cube for this

material is 4.97 Ångstroms, whereas for thorium it is 5.04. A few faint lines due to the lead slits appear in both portions. As the shadow of the filament is not apparent in the direct beam the positions of the lines were

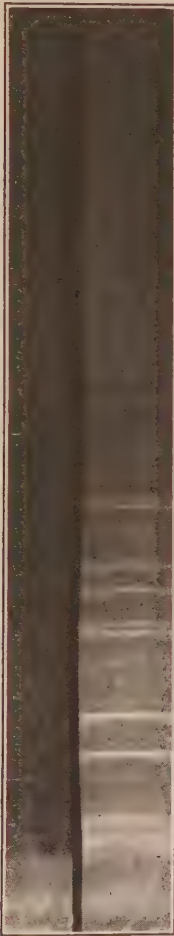


FIG. 2.

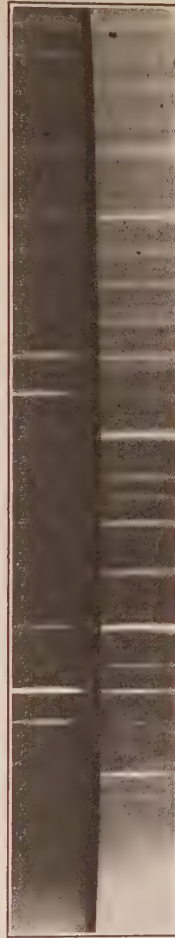


FIG. 3.

FIG. 2.—COMPARISON OF THORIATED FILAMENT AND POWDERED THORIA. NEGATIVE H-1: LEFT SIDE, FILAMENT, SINGLE STRAND SHOWING PATTERNS OF TUNGSTEN, THORIUM AND A NEW COMPONENT SEGREGATED TOWARD RIGHT END OF STRAND; RIGHT SIDE, POWDERED THORIA.

FIG. 3.—COMPARISON OF SHEET TUNGSTEN AND THORIATED FILAMENT. NEGATIVE H-107: LEFT SIDE, SHEET TUNGSTEN; RIGHT SIDE, MANY STRANDS OF FILAMENT, BOTH WRAPPED ON BRASS CYLINDER $\frac{1}{4}$ -IN. DIAMETER. EXPOSED WITHOUT FILTER.

measured from the upper edge of the undeviated beam and corrected for the actual position of the filament, and for a systematic error in the instrument, by checking the tungsten lines against a calibrating pattern made on the same instrument with a thin compressed specimen of finely divided

tungsten. The measured and corrected values, together with the theoretical values for tungsten, thorium, thoria and a face-centered cube with edge 4.97 Ångstroms, are given in Table 1. A reasonable interpretation of this peculiar pattern is that the specimen was segregated, the left-hand portion being tungsten plus a small amount of thorium and the right-hand portion an alloy of tungsten in thorium.

TABLE 1.—*Positions of Lines on Negative H-1, Left Side, in Millimeters*

Measured ^a	Corrected	Tungsten	Thorium	Thoria	F. C. C. Edge 4.97 Å	Remarks
28.0 R	28.4		28.1	25.2	28.4	
L 28.5	28.9					Lead slit
				29.2		
32.0 R	32.5		32.5		32.8	
L 32.8	33.2					Lead slit
L 36.0	36.5	36.6				
L 36.2	36.7	36.8				
				41.4		
L 45.5	46.1		46.1			
46.0 R	46.6				46.6	
L 46.6	47.2					Lead slit
				48.6		
				50.8		
L 51.1	51.8	52.0				
L 51.4	52.1	52.2				
L 53.8	54.5		54.3			
54.2 R	54.9				54.8	
54.8	55.5					Lead slit
L 56.0	56.7		56.6			
57.0 R	57.7				57.6	
				58.8		
L 63.0	63.8	64.0		63.9		
L 63.4	64.3	64.3		64.2		
			65.8			
				66.0		
					66.6	
			71.8			
				72.5		
71.8	72.8				72.8	
72.2	73.2		73.7?			Lead slit?
73.0	74.1	74.2				
73.5	74.6	74.5			74.5	
Beyond this value only tungsten lines are recorded.						

^a L indicates line in left portion only; R, in right.

In Fig. 3 is illustrated the comparison of patterns from many strands of the filament wound on a brass tube of 3 mm. radius, so as to form a

TABLE 2.—*Positions of Lines on Negative H-107, Right Side, in Millimeters*

Measured	Corrected	Tungsten	Thorium	F. C. C. Edge 4.97 Å	
32.2	32.2	32.0	28.1	28.4	
32.7	32.7	32.6	32.3		
		36.6	32.5	32.7	
36.8	36.8 ^a	36.8			
38.7	38.6 ^b				
44.8	44.6 ^b				
45.7	45.5	45.4	45.8		
46.5	46.3 ^a	46.3	46.1	46.5	
52.1	51.8	52.0			
52.5	52.2	52.2			
			53.9		
56.1	55.8	55.8		54.8	
57.2	56.9 ^a	56.9	56.6		
				57.6	
64.3	64.0	64.0			
64.8	64.5	64.3			
		64.6			
66.3	65.9	65.8	65.8		
				66.6	
72.9	72.5 ^a	72.5		72.4	
				72.8	
		73.9			
74.5	74.1	74.2	73.2		
75.2	74.8	74.5	73.7	74.2	
75.8	75.4 ^b			74.5	
79.0	78.5 ^b				
80.3	79.8	79.6			
			80.5		
81.8	81.3	81.2	81.0		
				82.2	
83.9	83.4 ^a	83.4			
84.5	84.0	83.8			
			85.6		
86.9	86.4	86.2	86.1		
				87.3	
88.8	88.3	88.1			
91.0	90.5 ^b				
92.3	91.8	91.6			
93.0	92.3 ^a	92.3			
		92.7			
		94.7	93.7		
95.2	94.6		94.3		
				95.6	
		98.6	98.2		
100.3	99.6	99.8	98.7		
101.0	100.1	100.1	99.7	99.8	
101.5	100.7 ^a	100.7	100.2	100.3	
101.8	101.0				Not in tungsten set
105.3	104.5	104.4		101.2	
106.8	106.0		106.1		Not in tungsten set
107.6	106.7	106.6			
		106.9			
108.5	107.6	107.5		107.8	
110.8	109.9	110.0			
			109.6		
			110.3		
			111.0	111.2	
			111.6	111.8	
113.2	112.2	112.3			
				112.8	
				113.2	
115.0	114.0 ^a	114.0			
115.8	114.8 ^a	114.8			
		115.2			
			116.3		
			117.2		
118.8	117.8	117.8			
				118.4	
				119.4	
121.0	120.0		120.3		Not in tungsten set
		120.5			
121.8	120.8 ^a	120.8	121.2		
122.7	121.6 ^a	121.6	121.6		
			122.5		
				122.2	
124.0	122.9			122.8	Not in tungsten set

TABLE 2.—(Continued)

Measured	Corrected	Tungsten	Thorium	F. C. C. Edge 4.97 Å	
		123.2		125.4 126.2	
128.5	127.3	127.2	126.7		
129.4	128.1 ^c	128.1	127.6		
				128.6 129.6	
131.7	130.3 ^c	130.3	130.4 131.4		
134.5	133.2	133.2		132.4 133.2	
135.0	133.7	133.9			
135.9	134.5	134.6 135.1			
			136.8 137.8		
		138.4			
		139.9		138.8 139.6	
141.4	140.0 ^c	140.0	140.1		
142.3	140.8 ^c	140.8	140.9 141.7 142.5		
144.6	143.0	143.2		142.4 143.2 143.6 144.6	
		144.6			
			146.2 147.3		
149.5	148.0	148.0			
150.8	149.2	149.0		148.8 149.4	
152.7	151.0		149.8 150.9		Not in tungsten set
153.6	152.0	152.1	152.1		
154.7	153.1 ^c	153.1		152.8 153.6 154.4	
			153.9		
			155.6 156.8		
159.6	158.0	157.4 158.1			
		158.6		158.2	
160.8	159.0	159.2	159.3 160.4 161.3	159.2	
163.8	162.0	162.3 162.9		162.2	
165.0	163.2			163.2 163.4	Not in tungsten set Not in tungsten set
165.7	164.0 ^c	164.0		164.4	
166.8	165.1	165.4	164.9		
168.4	166.7	167.0 167.3	166.0		
				167.7	
			168.3 169.3	169.1	
171.5	169.7	169.8			
173.0	171.0	170.8 171.3 171.6		171.4	
				172.6	
			174.0 175.2		
177.4	175.6 ^c	175.6			
		176.1			
178.7	176.8	176.8			

^b These lines were due to brass holder.^c These lines were used for calibration, hence values agree.

cylindrical specimen, and from a thin sheet of tungsten wrapped around the tubing. The black line separating the two patterns is curved because the lead septum in the instrument was slightly sprung. The relative intensities of corresponding tungsten lines in the two patterns are very different because the two types of forming operations have produced decidedly different grain orientations. This method of mounting gives effective focusing throughout the entire range, and at the same time presents a larger effective specimen surface for the larger angles where the ordinary patterns tend to become weak. A series of correction terms, which may be calculated from the position of tube, specimen and film and the size of the specimen, or may be secured from a calibration pattern, must be applied. The latter is the simplest way and in the present case the tungsten supplies its own calibration pattern. Since no filter was used, the tungsten pattern is complete, including not only the lines due to the alpha doublet usually used but also those from the beta and gamma waves. Many of the lines of the minor components differ so slightly from other lines of the tungsten pattern as to be indistinguishable, but a few for each are well removed or at least resolved from near-by tungsten lines. Seventy-one lines have been measured in this pattern. These,

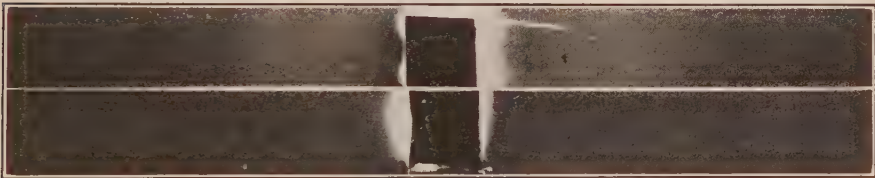


FIG. 4.—COMPARISON OF SHEET TUNGSTEN AND THORIATED FILAMENT AT LARGE DIFFRACTING ANGLES, SHOWING SCARCELY PERCEPTIBLE DIFFERENCES IN SPACINGS. UPPER HALF SHOWS FILAMENT; THE LOWER, SHEET TUNGSTEN.

with the corrected values, the theoretical values for tungsten, and the theoretical values for the alpha doublet lines of thorium and of the new component already observed in Fig. 2, are given in Table 2. It will be observed that there are three lines in each of these latter patterns which are distinctly visible and not coincident with lines from any other pattern. There can thus be no doubt of the presence of these components in the specimen represented. It is therefore reasonable to conclude that the new component is a characteristic structure, corresponding to a definite compound of tungsten in thorium, and not a special case of a whole series of solid solutions.

HOW MUCH THORIUM IS DISSOLVED IN THE TUNGSTEN?

A sensitive test for thorium dissolved in tungsten was applied. This consisted in reversing the diffractometer so that the diffracted beam

traveled backward almost along the incident beam. Under these circumstances the angle A in the diffraction equation

$$nL = 2d \sin A$$

is nearly 90° and the value of the angle changes greatly with a very slight change in the sine, hence with a very slight change in the spacing. As

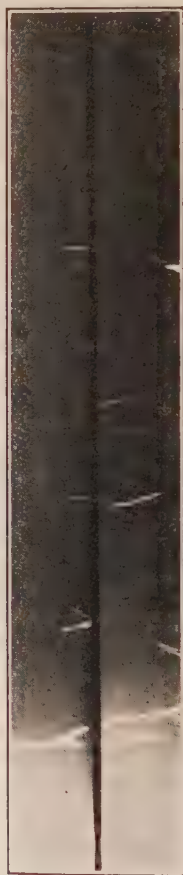


FIG. 5.—COMPARISON OF TWO ADJACENT PORTIONS OF A SINGLE-CRYSTAL FILAMENT OF TUNGSTEN AFTER DRAWING THROUGH A DIE. CRYSTAL HAS BEEN DISINTEGRATED AND SMALL CRYSTALS HAVE SLIPPED ON EACH OTHER.

shown in Fig. 4, there was no perceptible difference in the position of a pair of lines from pure tungsten and from the filament. Hence the amount of thorium dissolved in tungsten is inappreciable.

EFFECT OF COLD WORKING ON A SINGLE-CRYSTAL WIRE

During the investigation, some filaments were examined which had been made by drawing a single crystal of tungsten through a die. A typi-

cal example of the remarkable patterns is given in Fig. 5. The apparent strokes of lightning are due to diffraction of the Laue type from the series of small grains into which the crystal has been broken, each grain having been rotated slightly with respect to its neighbors. This suggests a most interesting mode of attacking the problem of torsional strain and slip in wires.

SUMMARY

The investigation shows that the major part of the thorium present in the so-called "thoriated-tungsten" filament is present as metallic thorium or as an alloy of tungsten in thorium, and not as thoria or an alloy of thorium in tungsten. It shows further that the alloy in question has a characteristic parameter and hence probably a characteristic composition. In the course of the investigation methods were devised for detecting as small an amount as 0.2 per cent. of a minor constituent.

DISCUSSION

P. P. TARASOV, Cleveland, Ohio (written discussion).—I should like to ask Dr. St. John how he explains the evidence given by the microscopic study on the presence of thoria in tungsten metal. It is well known that when thoriated tungsten ingot is polished the particles of thoria are readily seen under the microscope, and more so after slight etching. These particles are in the form of non-metallic gray globules. Their non-metallic nature is further indicated by their comparatively low plasticity; namely, on working tungsten ingots at very high temperatures, in the neighborhood of 1500°C ., they are somewhat elongated, together with tungsten grains, but when the working temperature is reduced to about 1000°C ., the elongated particles of thoria begin to break up with the brittle fracture typical of non-metallic substances.

In case metallic thorium is added to tungsten and then heat treated in the usual way, there is considerable loss of thorium, due to evaporation; the remainder of thorium turns into thoria. Whereas, when thoria is added to tungsten, the loss due to evaporation is very much less, and as the boiling point of thoria is much higher than that of thorium. It may be added here that oxygen for the formation of thoria from the thorium is supplied by a slight moisture content in the hydrogen.

The process of changing thorium into thoria can be interrupted before completion, in which case the microscope reveals a shell of non-metallic material resembling in every way material found in thoriated tungsten, and the core of metallic material which is undoubtedly thorium metal.

The shape of the particles of the material in question indicates that their melting point is much higher than that of thorium. The melting point of thorium metal is about 1830°C ., according to Marsh and Rentchler, while thoria melts in the neighborhood of 3000°C .

Hardness of those gray particles always found in thoriated tungsten ingots is another evidence of their non-metallic nature. Thorium metal is not very hard, softer than tungsten, while thoria, being metallic oxide, naturally must be much harder. When thoriated tungsten is polished, sometimes slight polishing scratches remain on the surface. These scratches never pass across thoria particles, indicating that those particles must be harder than surrounding matrix of tungsten metal.

It seems that when X-ray evidence is at variance with so much other evidence, some of which is of a very positive character, such X-ray evidence should be very clear and definite, which Dr. St. John's evidence seems not to be.

L. W. MCKEEHAN, New York, N. Y.—I should like to question Dr. St. John in regard to the size of filament that contained thorium, because the absorption of these metals is so great for the molybdenum radiations that unless the filament is quite small, say below 2 mils in diameter, the surface is responsible for a great deal of the effect observed, and there is always a possibility of a little variation in distribution of intergranular materials between the surface and the center of wire that has been drawn.

Another question is whether the filament was, as I suppose it must have been, in the original hard-drawn state or whether it had been glowed. In the latter case I should suppose that the distribution of thorium again would be affected. Last winter some photographs were shown of thoriated filaments glowed for long periods, in which the surface appeared to have been cleaned of thorium. At least that was the interpretation given, the central part containing the specks of thorium—or whatever it is—a clear zone lying next and the pitted surface outside that. If the wire was merely cold drawn, such a variation in content from center to surface would not be expected.

In regard to the photograph showing the "lightning flashes," there was a note by Yoshida and Tanaka² in which similar appearances were produced by applying the Laue method to what were supposed to be single-crystal wires. The explanation is that different parts of the length of a single crystal exposed to the X-ray beam will reflect the various wave lengths present in different directions, so that the whole wire gives as a reflection a stripe somewhere on the plate, not necessarily parallel to the specimen itself. The parts of this image are due to wave lengths that are different. It is possible that some of the effects shown here are due to the same cause, because we know that in the X-radiation used here there is a good deal of general radiation able to produce something very much like the Laue pattern.

E. P. CHARTKOFF, Cleveland, Ohio.—In accordance with the degree of precision that X-ray analysis affords, would the author give more exact data on the conditions under which the tests were made in order that the conclusions arrived at might be more clearly comprehended? I was rather interested to know just what state of filtering existed, particularly in the left-hand side of Fig. 2, the film of the thoriated filament. Also, would he explain just how the intersection of the film with the cones of diffraction could give such a pattern as he has shown where one constituent in the beam gives lines going clear across the film and another constituent in the beam gives lines which traverse the film only in a limited and definite amount.

S. L. HOYT, Schenectady, N. Y.—Dr. St. John's paper, I believe, is really more limited than the title would lead one to suspect. The paper ostensibly deals with the condition of thorium in thoriated tungsten filaments but the evidence is that obtained by X-ray analysis. I think we should bear that distinction in mind.

To one who has done any considerable amount of work on this subject, using the methods of microscopic and chemical analysis, the conclusions which Dr. St. John reaches are, I would say, somewhat startling.

There is nobody who regards any more favorably and highly than I the results of X-ray analysis as applied to the study of metallurgical problems. We certainly have there a very important tool. On the other hand, it is limited and many times, as I believe in the present case, it is necessary to consider the general problem from other angles in order to arrive at the final conclusion.

² U. Yoshida and K. Tanaka: Laue Photograph Taken with a Long Slit. *Nature* (1926) 118, 912.

For instance, the author draws the conclusion, which of course is rather guarded, that the thorium content as ThO_2 is under 0.2 per cent. That is certainly in direct variance with the microscopic examination. The reason for that I would not attempt to account for, but I have examined thoriated filaments which run from 0 per cent. of thoria to 2 per cent. of thoria, and the microscope shows a definite quantitative increase in the amount of this constituent to which Mr. Tarasov referred. The micrographic method of determining the thoria content can be carried out very easily and the results checked with those of chemical analysis, in which case the thoria is determined as a non-volatile residue. Both methods are customarily employed.

Furthermore, he has referred to the fineness of subdivision of the thoria. It is safe to assume that the thoria present is in as fine a state of subdivision as is possible to produce it, so we may assume that the thoria particles present are extremely finely subdivided. That may possibly be the leading reason for the failure to secure strong thoria lines from a filament that is supposed to contain 0.75 per cent. thoria. Dr. St. John is very frank in his reason why the evidence on this point is negative.

Even though metallic thorium be added to tungsten, the evidence is very strong, and to my mind, very clear that the thorium is oxidized during the process to thoria, and the end is practically the same thing; that is, thoria particles in tungsten. There may be a small amount of metallic thorium in solution in the tungsten and that can be determined by means of the electric conductivity and the temperature coefficient.

The author also refers to the amount of thorium dissolved in tungsten in a thoriated tungsten filament. That thorium is simply the thorium that is reduced, according to the Langmuir hypothesis, by the tungsten present, and on that basis we would expect only an exceedingly small amount of metallic thorium.

Summarizing this discussion, I would say that the X-ray analysis presented by Dr. St. John does not seem to me to be at all final, and that in the face of other evidence which has been obtained over a period of years the conclusions which he reaches are certainly at variance with a large amount of information which has been obtained by microscopic and chemical means.

Z. JEFFRIES, Cleveland, Ohio.—I think Dr. St. John can rest assured that his parameter measurement would not vary materially whether the sheet contained 0.75 per cent. thoria or not.

Mr. Davis has covered that subject very thoroughly in a paper published by the American Physical Society, in which he shows that the parameters of so-called pure tungsten are substantially the same as we would expect, with only 0.002 to 0.004 per cent. thorium in solid solution according to the constitution as postulated previously.

The presence of metallic thorium in the absence of any oxygen definitely yields a material having a higher cold resistance than thoriated tungsten, and having a lower ratio of hot to cold resistance; in other words, definitely yields a material indicative of a solid solution.

A. ST. JOHN.—Mr. Tarasov says that when a thoriated tungsten ingot is polished and examined under the microscope "the particles of thoria" are readily seen and appear as "non-metallic gray globules." He also says "their non-metallic nature is further indicated by their comparatively low plasticity" and elaborates that idea. I would remind him that when the original paper by Jeffries and Tarasov was presented, in February, 1927, Dr. Jeffries himself suggested that there were some reasons for thinking these particles might be an inter-metallic compound. This statement and my comment that the X-ray evidence confirmed it were omitted from the published discussion.

To my mind, the other evidence asserted by Mr. Tarasov is equally indicative that the gray globules are not thoria. I am under the impression that finely divided thoria

is white, not gray, whereas finely divided thorium is bluish gray. It is well known that thorium oxidizes readily and it is reasonable to believe that any particles of thorium laid bare in preparing the specimen would be slightly oxidized and present the blue-gray appearance characteristic of a metal with a very thin oxide film instead of the bright metallic appearance.

Furthermore, the fact that in the sintered ingot the particles are globular suggests that they have been fused, an operation more to be expected for thorium than for thorium under usual sintering practice.

With respect to Mr. McKeehan's question, the filament was very fine. It was almost invisible and very difficult to handle on account of its fineness. It was the filamentary material that is used in making up filaments for radio tubes and was in the original state as manufactured; had never been removed from the original spool until I removed it.

With respect to the question concerning Fig. 2, instead of having a specimen going entirely across the beam, the specimen only occupies one-half of the beam, say the right-hand half, and the pattern is going to tend to be concentrated in the right-hand half of the diffractometer. If the specimen goes clear across the space, the pattern will be distributed and the lines will go clear across.

In order to check that, I have made up some specimens in which I have had the specimens stop midway or three-quarters of the way and that shows up very decidedly. It was on that account that I finally came to the conclusion that the only reasonable explanation of the peculiar appearance of one side of Fig. 2 is an actual segregation. At first it seemed to be a very forced explanation.

With respect to Mr. Hoyt's remarks as to the microscopic evidence, personally I do not believe anybody has ever seen any metallic thorium in a specimen prepared under the microscope. You almost always are seeing an oxidized surface.

X-ray Analysis of Plastic Deformation of Zinc

BY T. A. WILSON* AND S. L. HOYT,* SCHENECTADY, N. Y.

(Detroit Meeting, September, 1927)

THE plastic deformation of slender single crystals of zinc has been described in some detail in the paper by Mark, Polanyi and Schmid,¹ which has become a classic, and also by one of the present authors in a somewhat shorter account.² The study of single-crystal zinc is termed classical because zinc single crystals offer, perhaps, the best material yet available for the study of atomic behavior during deformation and the effect known as "strengthening" in metals.

A considerable amount of additional work has also been done on single-crystal zinc, but as it is not closely related to the present paper it will not be considered. Throughout all the former work, the mechanism of plastic deformation first described by Mark, Polanyi and Schmid has been assumed to hold. This may be said to offer the strongest confirmation of its correctness. Even so, the picture of the process has never been as completely portrayed as is desirable. The first object of the present paper is to describe work that has been done in this field, and which is even yet being carried on, in the hope that a more complete picture may be obtained.

Mathewson and Phillips³ have recently described a new mechanism of the deformation of zinc based on their study of large rectangular crystals. One of their conclusions was that deformation produced twinning with a rotation of some of the basal planes into positions 94° removed from their original position; a position almost the same as that of the prismatic planes before twinning. A second conclusion was that fracture occurred along these basal planes in their new position, and, therefore that fractures previously regarded as prismatic were in reality basal. Such findings are of great significance and they raise a question as to the generality of such behavior. Professor Mathewson's opinion is that even the slender cylindrical single crystals behave in the same manner as his large rectangular crystals when strained by simple tension.

* Research Laboratory, General Electric Co.

¹ H. Mark, M. Polanyi and E. Schmid: Beschreibung der Erscheinungen und Untersuchungsmethoden. *Ztschr. Physik.* (1922) **12**, 58.

² S. Hoyt: Plastic Deformation of a Zinc Single Crystal. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 116.

³ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 143.

The second object of this paper is to subject both the classical theory and this more recent theory to a searching inquiry to determine the validity of each. Fortunately, each theory presents a definite picture of atomic arrangements, therefore the problem is one that can be attacked with present methods of X-ray analysis with chances of success.

The third object of this paper is to describe in greater detail than has yet been done the true condition of the zinc crystal during deformation, and hence to show the extent of the preservation of the lattice structure, and of the occurrence of warping and fragmentation. The major features of the deformation of zinc have been fully reported in the papers referred to. That portion of the subject will not be reviewed here. It will also be accepted that zinc possesses the hexagonal close-packed structure with an axial ratio of 1.86.⁴ Accordingly, the planes of greatest interplanar distance are the basal planes.

The subject will be treated under the following headings: (1) The plastic deformation of polycrystalline zinc strip; (2) the plastic deformation of a single-crystal zinc wire, and (3) the fracture of single-crystal zinc specimens.

CHARACTERISTICS OF THE SPECTROGRAMS TO BE EXPECTED FROM EACH THEORY

In working with the polycrystalline zinc strip, the monochromatic pinhole method described by Clark, Brugmann and Heath⁵ was employed. The two mechanisms of deformation would produce widely different spectrograms from plastically deformed zinc strips, so that the mechanism of elongation should be definitely settled by this means. This will be evident from the following explanation.

If the planes of a particular family occupy only one position relative to the incident X-ray beam, and if the angle between the planes and the beam is such that Bragg's law of reflection⁶ is satisfied, a single spot will appear on the film from this family of planes at a fixed radial distance from the zero-beam impression. If this family of planes maintains the proper angle with respect to the incident beam, it may be rotated any amount about the incident beam as an axis, and reflection will result; but the reflected beam is always in a plane that includes the normal to the plane and the primary beam.⁷ Consequently, the reflection will

⁴ R. W. G. Wyckoff: *International Critical Tables* (1926) **1**, 341; A. W. Hull: X-ray Crystal Analysis of Thirteen Common Metals. *Phys. Rev.* (1921) **17**, 571.

⁵ G. L. Clark, E. W. Brugmann and S. D. Heath: New X-ray Studies of the Ultimate Structures of Commercial Metals. *Jnl. Ind. Eng. Chem.* (1925) **17**, 1142.

⁶ W. H. and W. L. Bragg: *X-Rays and Crystal Structure*, 20. Bell & Sons, London (1915).

⁷ J. D. Bernal: The Interpretation of X-ray Single Crystal Rotation Photographs. *Proc. Roy. Soc.* (1926) **113 A**, 117.

generate a circle on the film with the primary beam as a center. Further, if the planes of the family which are in a position to reflect are limited to certain directions about the primary beam, the circle will degenerate into a set of arcs, each arc showing the location of a certain group of planes. If, as usually happens, there are some planes suitable for reflection at all positions about the zero beam, but with increased concentration of these planes in certain directions, the circle will show itself complete, but the density of the reflection on the film will be greater in those directions in which most of the planes are situated.

Let us consider the case in which basal planes are initially lying flat in the horizontal surface of the specimen. Following the twinning action, according to the theory of Mathewson and Phillips, some of these planes at least will have rotated into positions 4° removed from a vertical

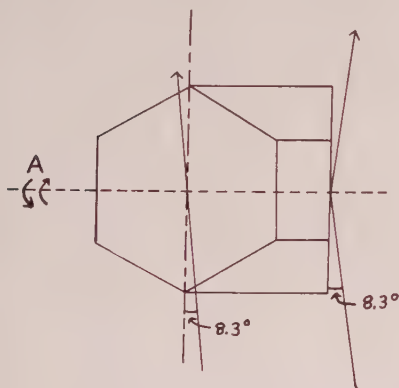


FIG. 1.—ORIENTATION NECESSARY FOR TWINNED BASAL REFLECTION.

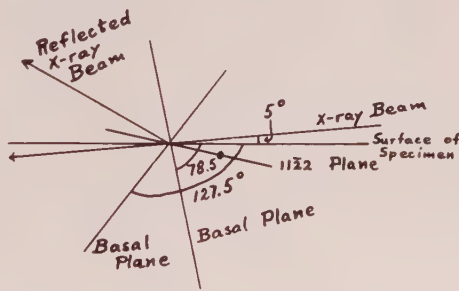


FIG. 2.—RELATIONS BETWEEN SURFACE OF SPECIMEN AND BASAL PLANE FOR 1122 REFLECTION.

direction. Therefore, if it can be shown that some of the basal planes fulfill the conditions of the Bragg reflection law, both before and after the twinning action, increased density of reflection from basal planes should be observed at a point on the circle of reflection 94° removed from the original reflection. As the deformation of the zinc strip is increased, the successive twinings produced in the elementary prisms cause the basal planes to be oriented more and more at random. Accordingly, the circle of basal-plane reflections loses its maxima and approaches the condition of even intensity, the sign of random orientation.

On the other hand, the classical theory of plastic deformation would lead us to expect that the reflection maxima would endure throughout the deformation. It might even be the case that the maxima would become more centralized due to the swinging into line of the basal planes.

It remains to be shown that in a specimen of strip zinc, some of the basal planes, at least, are in such a position that reflections from twinned

positions could be detected should twinning occur. The basal reflections recorded on the films (see Figs. 4, 5, 7 and 8) with the greatest distinctness are of the second order.

The second-order reflection occurs with an angle between the incident and the reflected X-ray beams of 16.6° . The plane, therefore, must make an angle of 8.3° with the X-ray beam before reflection can occur. In order that the basal plane formed by twinning shall produce reflection, the original basal plane must be turned so that the hexagonal axis parallel to the twinned basal plane forms an angle of 8.3° with the X-ray beam (see Fig. 1). It can be turned in either direction about the normal to the twinned basal plane, as shown by the arrows at *A* without disturbing this condition. If it is turned far enough, reflection will result from some $11\bar{2}$ -*y* plane. The first plane of this kind to produce reflection is the $11\bar{2}2$ plane,⁸ which reflects with an angle of 35.6° between the primary and reflected beams.

The plane, accordingly, makes an angle of 17.8° with the X-ray beam. Table 1 shows that the angle between this plane and the basal plane is 61.7° .

TABLE 1.—*Angles Useful in Solving X-ray Spectrograms of Zinc*

Reflecting Plane	Angle Between			
	Reflecting Plane and Basal Plane Degrees	Reflecting Plane and X-ray Beam Degrees	Basal Plane and X-ray Beam Degrees	Surface of Specimen and Basal Plane Degrees
0001 (2)	0	8.3	8.3	81.7
10 $\bar{1}0$	90	8.9	81.1	8.9
10 $\bar{1}1$	65	9.9	55.1–74.9	34.9–15.1
10 $\bar{1}2$	47	12.3	34.7–59.3	55.3–30.7
0001 (3)	0	15.6	15.6	74.4
11 $\bar{2}0$	74.8	15.6	59.2–90.4	30.8–0.6
11 $\bar{2}2$	61.7	17.8	43.9–79.5	46.1–10.5
20 $\bar{2}1$	76.2	16.9	59.3–93.1	30.7–6.9

In the experiments described in this paper, conducted with a monochromatic pinhole beam of X-rays, the beam was usually caused to graze the surface of the strip with an angle of incidence of 5° . According to the construction shown in Fig. 2, reflection from the $11\bar{2}2$ plane would correspond to an angle between the surface of the specimen and the basal plane of either 78.5 or 127.5° . The grazing-beam photographs reproduced in Figs. 4, 5, 7 and 8 show that some reflections were obtained from this plane; but unless the original basal planes are in such positions

⁸ W. M. Peirce, E. A. Anderson and P. Van Dyck: An Investigation of the Alleged Allotropy of Zinc by X-ray Analysis and a Redetermination of the Zinc Lattice. *Jnl. Frank. Inst.* (1925) **200**, 349.

that basal reflections or $11\bar{2}2$ reflections are obtained, penetration of the specimen by X-rays must be resorted to.

In this method, the X-ray beam penetrates the specimen normal to its surface, causing reflections from basal, prismatic and pyramidal planes. The disposition of the basal planes, for example, along any particular diameter of this type of pattern can then be computed from appropriate reflections from other planes, provided the angles between these planes and the basal planes are known. This information, useful in solving penetrating beam patterns, has been collected in Table 1. The patterns reproduced in Figs. 3 and 6 are of this kind, but a discussion of their solution will best be deferred until the experimental details are taken up. It may be said here that these photographs show many basal planes properly oriented in the strip to give reflections from the twinned positions on the glancing-beam patterns, if the deformation has produced such new orientations.

This will probably be sufficient to characterize the first test, as listed in Table 2. The second characteristic of the X-ray patterns follows at once after a little consideration. According to the classical theory, as is well known, deformation promotes the achievement of a certain average orientation of the slip planes. The newer theory, on the other hand, would require a new set of basal planes at 94° to the original set as a consequence of twinning. In terms of the symmetry of the pattern we should expect a twofold symmetry if the classical theory holds, and at least a fourfold symmetry, if the twinning theory is correct.

Considerations of Laue spectrograms (polychromatic radiation) obtained from deformed single crystals, are even more conclusive. According to the classical theory of deformation, because of the accompanying distortion of the lattice, the spectrogram of such a crystal should show the existence of fourth-order bands with an apparent increase in its natural symmetry.⁹ On the basis of the twinning hypothesis, the Laue pattern should approach a smear, produced by reflections of the different wave lengths from many planes at many different angles.

The cleavage faces of fractured single-crystal samples have also been investigated by allowing the X-ray beam to glance over the surface. One of the samples was cylindrical and made by the Czochralski method,¹⁰ while the other was a large crystal similar to those described by Mathewson and Phillips,¹¹ and kindly supplied by Dr. Mathewson. These

⁹ E. Schiebold: Die Verfestigungsfrage vom Standpunkt der Röntgenforschung. 1.-Der Mechanismus der Verformung kristalliner Medien und seine Kennzeichnung im Röntgenbild. *Ztschr. Metallk.* (1924) **16**, 417.

¹⁰ J. Czochralski: Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle. *Ztschr. phys. Chem.* (1917) **92**, 219.

¹¹ C. H. Mathewson and A. J. Phillips: *Loc. cit.*

spectrograms show which lattice planes are parallel to the surface, or cleavage face. The results came out as would be predicted from the classical theory, for they show that in the former case the prismatic plane is parallel to the surface, while in the latter, as is required by the twinning hypothesis, both basal and prismatic planes are present.

STUDY OF POLYCRYSTALLINE ZINC STRIP

Two specimens of strip zinc were experimented with, both having been kindly supplied by A. P. Knight of the Rome Manufacturing Co. The parent piece was 13 mils thick, and had been rendered ductile by

TABLE 2.—*Characteristics of X-ray Patterns Obtained on Basis of Each Theory of Plastic Deformation*

CLASSICAL THEORY	TWINNING THEORY
Polycrystalline Deformation	
Deformation great: Monochromatic pin-hole pattern, symmetry low, concentration of planes about certain zones produced by slipping and rotation.	Deformation great: Monochromatic pin-hole pattern, random orientation, produced by successive twinings.
Deformation slight: Monochromatic pin-hole pattern, symmetry low.	Deformation slight: Monochromatic pin-hole pattern, symmetry higher, probably 4-fold.
Single-crystal Deformation	
Laue pattern, appearance of fourth-order bands.	Laue pattern, development of smear.
Single-crystal Fracture	
Glancing-beam pattern, prismatic plane shown parallel to fractured surface.	Glancing-beam pattern, basal plane shown parallel to fractured surface.

appropriate heat and mechanical treatments. The second piece was derived from this one by rolling a sample to a thickness of 4 mils on the precision rolls of the General Electric Research Laboratory. The direction of rolling of the parent strip was maintained. This was done at room temperature, and may be considered as a proof that the strip was ductile. In accordance with the scheme outlined above, three photographs were taken of each sample by the monochromatic pinhole method, with the sample in three different positions relative to the beam. Fig. 3 shows the photograph of the 13-mil strip taken with the beam penetrating the sample, and Figs. 4 and 5 show the patterns obtained with the beam grazing the surface parallel to and perpendicular to the direction of rolling, respectively. Figs. 6, 7 and 8 show the same conditions for the 4-mil strip. The surfaces were carefully etched with hydrochloric acid, before making the photographs, to eliminate purely surface effects. On the penetrating-ray photographs, the vertical direction on the film is parallel to rolling.

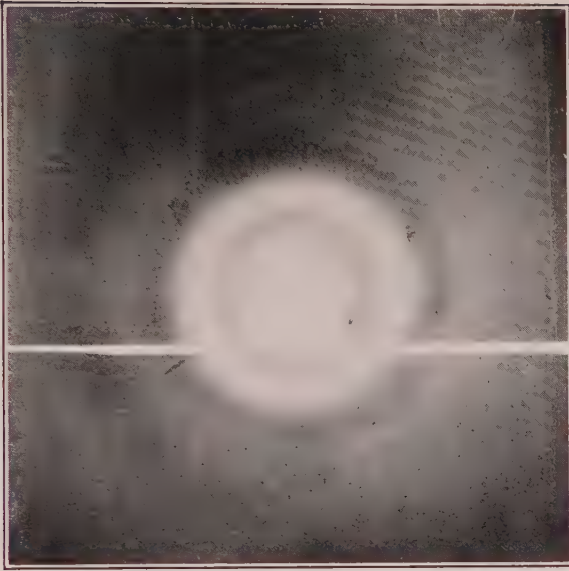


FIG. 3.—13-MIL DUCTILE ZINC, PENETRATING BEAM, ROLLING DIRECTION VERTICAL.

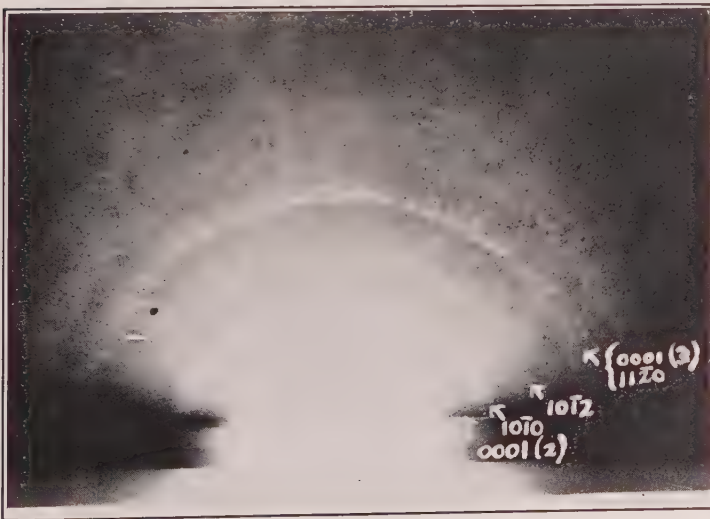


FIG. 4.—13-MIL DUCTILE ZINC, GRAZING BEAM PARALLEL TO ROLLING DIRECTION.

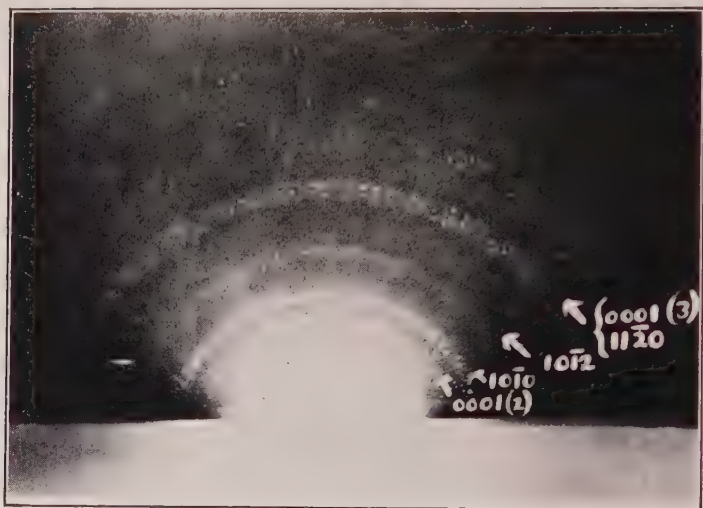


FIG. 5.—13-MIL DUCTILE ZINC, GRAZING BEAM PERPENDICULAR TO ROLLING DIRECTION.

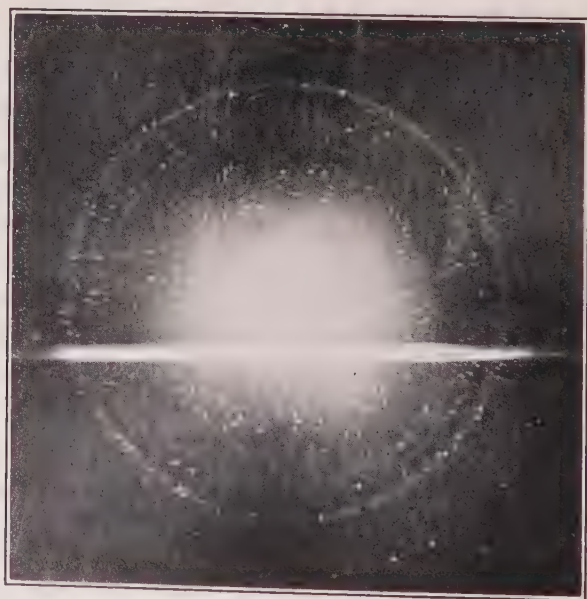


FIG. 6.—4-MIL DUCTILE ZINC, PENETRATING BEAM, ROLLING DIRECTION VERTICAL.

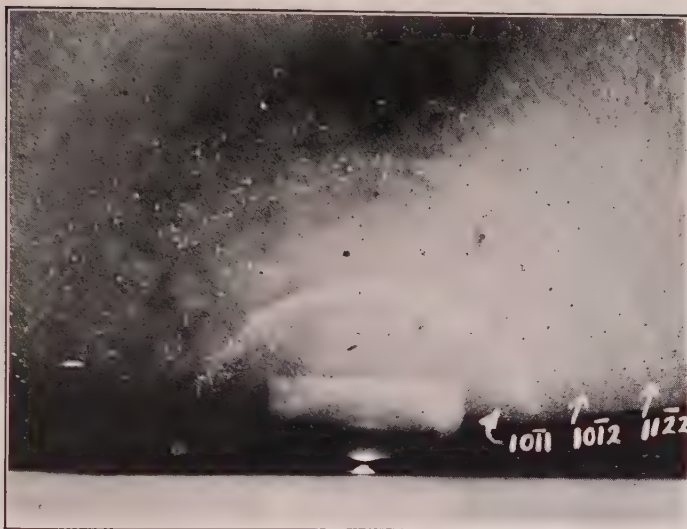


FIG. 7.—4-MIL DUCTILE ZINC, GRAZING BEAM PARALLEL TO ROLLING DIRECTION.



FIG. 8.—4-MIL DUCTILE ZINC, GRAZING BEAM PERPENDICULAR TO ROLLING DIRECTION.

Table 3 gives the analysis of Fig. 3. The film shows the strained condition of the metal, which is to be expected as the result of rolling, by the presence of bands instead of spots. It also shows an even distribution of reflections from the pyramidal and prismatic planes. In view of the considerations advanced in explanation of Fig. 1 and from the hexagonal symmetry of the zinc lattice, special interest attaches itself to the reflections from the $10\bar{1}0$ and $10\bar{1}1$ planes at an angle of about 38° each side of the diameters representing the direction of rolling and the perpendicular direction respectively. The strength of the reflections along these lines shows that there are basal planes so oriented in the specimen that they would give twinned basal reflections in the glancing-beam photographs, if twinning had taken place. It is reasonable to suppose that some of the planes giving basal reflections are also in the proper position.

TABLE 3.—*Spectrogram of 13-mil Ductile Zinc, X-ray Beam Penetrating Specimen*

Direction of Rolling Vertical.			Distance from Specimen to Film, 95 Mm.		
Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Planes
12	0.126	7.2	3.6	8.3	0001 (2)
to	to	to	to	8.9	$10\bar{1}0$
34	0.358	19.9	10.0	9.9	$10\bar{1}1$

The analyses of Figs. 4 and 5 are recorded in Tables 4 and 5, respectively. The extent of the arc of maximum intensity in each case is measured from the left horizontal radius of the film, as is shown in Fig. 9. According to the previous explanation, the maximum corresponds to the orientation at which the planes giving that reflection are concentrated. In testing the twinning hypothesis, we may well consider two cases; simple twinning and multiple twinning. The relationship between the two becomes apparent after a brief consideration of the twinning hypothesis, but perhaps we can do no better than to quote Dr. Mathewson in this connection:¹² "The first, or primary, twinning may set up 6 new orientations. Each of these new orientations may then undergo a secondary twinning, which will account for 36 additional orientations, of which 6 merely represent a return to original conditions. There are thus $30 + 60 + 1$ orientations possible after secondary twinning. The third twinning stage will produce 150 additional orientations, and a fourth twinning stage 750. After 7 stages of twinning, if such is possible, we may have over 100,000 new orientations. All of these must be

¹² Correspondence with the authors.

arranged according to hexagonal symmetry, but they do in effect represent something very close to random orientation."

TABLE 4.—*Spectrogram of 13-mil Ductile Zinc, X-ray Beam Glancing the Surface of Metal at Five-degree Angle, Parallel to Direction of Rolling*
Distance from Specimen to Film, 70 Mm.

Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Angles of Maximum Intensity, Degrees	Planes
21	0.299	16.6	8.3	8.3	83-100	0001 (2)
24	0.343	19.0	9.5	8.9	Complete arc	10 $\bar{1}$ 0
31	0.441	26.0	13.0	12.3	37-155	10 $\bar{1}$ 2
41	0.585	30.2	15.1	15.6	Almost complete arc	0001 (3) 11 $\bar{2}$ 0

TABLE 5.—*Spectrogram of 13-mil Ductile Zinc, X-ray Beam Glancing the Surface of Metal at Five-degree Angle, Perpendicular to Direction of Rolling*
Distance from Specimen to Film, 70 Mm.

Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Angles of Maximum Intensity, Degrees	Planes
21	0.299	16.6	8.3	8.3	57-113	0001 (2)
24	0.343	19.0	9.5	8.9	40-135	10 $\bar{1}$ 0
31	0.441	26.0	13.0	12.3	25-145	10 $\bar{1}$ 2
41	0.585	30.2	15.1	15.6	Almost complete arc	0001 (3) 11 $\bar{2}$ 0

TABLE 6.—*Spectrogram of 4-mil Ductile Zinc, X-ray Beam Penetrating Specimen*

Direction of Rolling Vertical. Distance from Specimen to Film, 95 Mm.

Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Planes
14	0.148	8.5	4.2		
to	to	to	to	8.3	0001 (2)
28	0.296	16.5	8.3		
31	0.326	18.0	9.0	8.9	10 $\bar{1}$ 0
34	0.358	19.9	9.9	9.9	10 $\bar{1}$ 1
43	0.453	24.5	12.2	12.3	10 $\bar{1}$ 2

If simple twinning had occurred, a fourfold symmetry of the basal arcs would be evident. But although there were basal planes favorably

disposed to show this twinning, fourfold symmetry is lacking from the second-order reflections, both in the direction of rolling and in a transverse direction. In Fig. 5, the result of establishing fourfold symmetry in the second-order reflections would have been an arc showing nearly uniform intensity, because of an overlapping of maxima. If multiple twinning had occurred, the arc would show uniform intensity as a result of random orientation. It is true that the third-order reflection is of almost even intensity, but this arc is formed by reflection from two planes, which serves to decrease its importance. From the second-order reflection, therefore, it is clear that a concentration of the basal planes occurs but at one place, and not at two or more as is required by the twinning hypothesis, so that we may conclude that twinning as a result of plastic deformation is negligible in the 13-mil zinc strip.

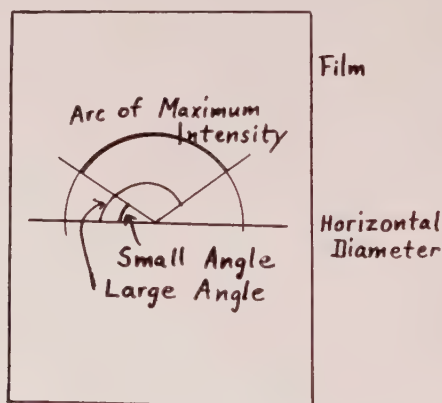


FIG. 9.—METHOD OF MEASURING ARC OF MAXIMUM INTENSITY.

The penetrating-ray picture of the 4-mil specimen (Fig. 6) shows twofold symmetry. The analysis of this film in Table 6, which applies to the top half only, by reference to Table 1, shows that there are basal planes making both large and small angles with the surface both in the direction of rolling and in a transverse direction. The analysis also shows that there are basal planes present which satisfy the requirement for reflection from the twinned basal planes, were any present.

But again no evidence of twinning is found. The photographs obtained with the 5° glancing beam, shown in Figs. 7 and 8, are analyzed in Tables 7 and 8. Fig. 7 shows no basal reflection. Fig. 8 shows a decided maximum in the second-order basal reflection, but fourfold symmetry is not visible. The results of the 4-mil specimen are readily to be interpreted on the basis that the basal planes are arranged about a direction parallel to rolling, so that they make angles of 22° to 48° with respect to the surface, and in a transverse direction, so that they make angles less than 8° with respect to the surface. In addition, if the

hexagonal axes of these planes in the direction of rolling are rotated nearly into the direction of tension, a maximum reflection from the $10\bar{1}1$ plane would be expected. This is obtained, as is shown in Fig. 8 and Table 8.

As soon as this lattice arrangement was known, it was predicted that this strip would be strong and comparatively brittle in a transverse direction, and weak and comparatively ductile in a longitudinal direction. Subsequent tests verified the prediction completely.¹³

In conclusion, it can be said that no evidence of twinning has been found in either of the polycrystalline zinc strips subjected to plastic deformation. On the other hand, the results agree with the classical theory.

TABLE 7.—*Spectrogram of 4-mil Ductile Zinc, X-ray Beam Glancing the Surface of Metal at Five-degree Angle, Parallel to Direction of Rolling*
Distance from Specimen to Film, 75 Mm.

Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Angles of Maximum Intensity, Degrees	Planes
27	0.360	19.9	9.9	9.9	On left	$10\bar{1}1$
35	0.466	25.0	12.5	12.3		$10\bar{1}2$
47	0.626	32.0	18.0	17.8		$11\bar{2}2$

TABLE 8.—*Spectrogram of 4-mil Ductile Zinc, X-ray Beam Glancing the Surface of Metal at Five-degree Angle, Perpendicular to Direction of Rolling*
Distance from Specimen to Film, 75 Mm.

Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Possible Angle of Reflection, Degrees	Angles of Maximum Intensity, Degrees	Planes
22	0.293	16.3	8.2	8.3	42-68	0001 (2)
24	0.320	17.8	8.9	8.9		$10\bar{1}0$
27	0.360	19.9	9.9	9.9	70-122	$10\bar{1}1$
35	0.466	25.0	12.5	12.3	80-100	$10\bar{1}2$
47	0.626	32.0	16.0	15.6		0001 (3)
						$11\bar{2}0$

STUDY OF SINGLE-CRYSTAL ZINC

The crystal used in this study was about 1 mm. in diameter and 50 mm. long, grown from the melt by the Czochralski method. It was stretched by simple tension, first into a flat ribbon of elliptical cross-section, and then into an after-elongation thread of circular cross-section.

¹³ See also C. H. Mathewson and A. J. Phillips: *Loc. cit.*



FIG. 10.—PHOTOMICROGRAPH OF DEFORMED ZINC CRYSTAL.

The surface appearance of this crystal at the junction of the ribbon and thread is given in Fig. 10. X-ray photographs were taken of this crystal at various places along the length with the rays penetrating the specimen. The preservation of the regular atomic arrangement is evidence of simple atomic displacements required by the classical theory. These photographs show, even in the after-elongation thread, a remarkable preservation of this regularity. (See Table 2.)

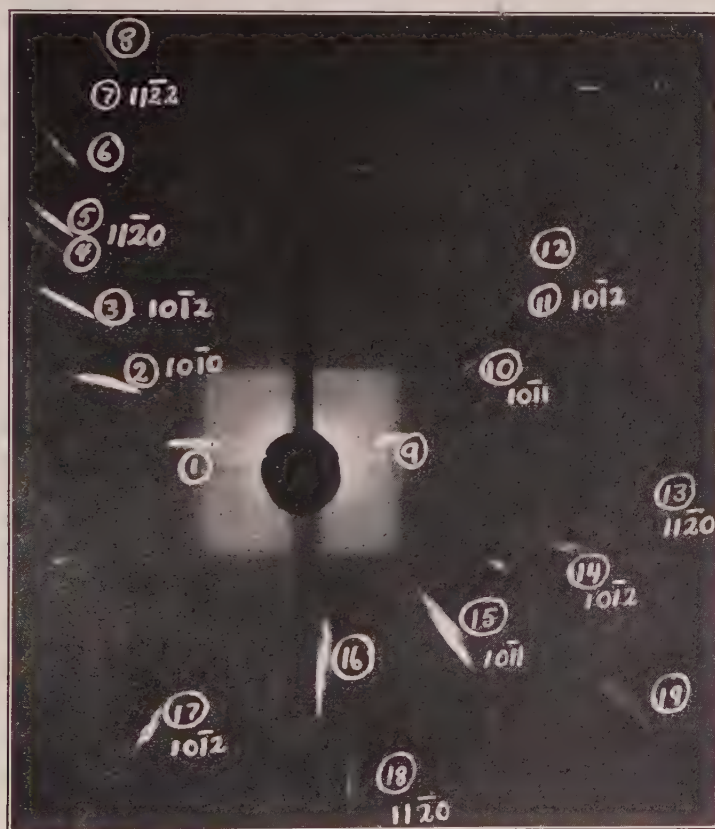


FIG. 11.—RIBBON OF DEFORMED ZINC SINGLE CRYSTAL—I.

Two spectrograms were made of the ribbon section of the deformed crystal. Fig. 11 shows the pattern obtained by the monochromatic pinhole method at a point one-half inch from the thread. Fig. 12 shows that obtained by the Laue method quite close to the thread.

The readings obtained from Fig. 11 are tabulated in Table 9, the spots of the photograph being numbered to correspond to the lines of the table. In this experiment the zinc crystal was clamped in the vertical direction in the path of the X-ray beam, so that the crystal made an angle of 85°

with respect to the beam. The after-elongation thread was at the top. The film was perpendicular to the X-ray beam (Fig. 13). The direction of the crystal is shown by the shadow across the light square in the center, below the circular image of the shield. This shield consisted of a lead button hung in front of the film to prevent the primary beam from reaching the film and producing fog. Such protection of the film was necessary

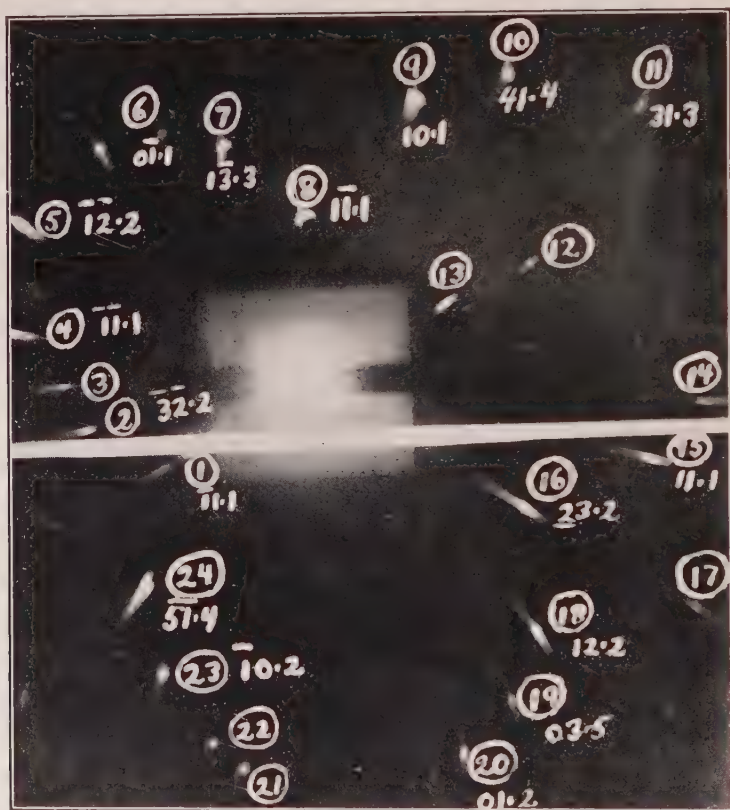


FIG. 12.—RIBBON OF DEFORMED ZINC SINGLE CRYSTAL—II.

in all of these experiments because the beam of X-rays was actually wider than the crystal.

The determination of the positions of the spots in such a spectrogram presents great difficulty because the spots are elongated into fourth-order bands. The position of maximum intensity of each band was the one chosen for the true position of the spot. Spots 9, 15, 16 and 18, lying as they do in different directions throughout the specimen, were used to determine the position of the hexagonal axis; but to fix uniquely the position of the elementary prism in space, in addition to the location of

the hexagonal axis, the amount of rotation of the prism and the direction of the axis about which this rotation has occurred must be specified

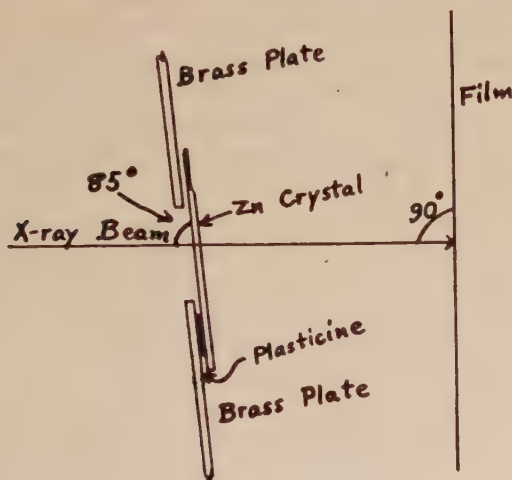


FIG. 13.—RELATIVE POSITION OF CRYSTAL, BEAM AND FILM IN FIGS. 11 AND 20.

with reference to some standard position. The position considered as standard is that in which the trigonal axis and the X-ray beam are parallel.

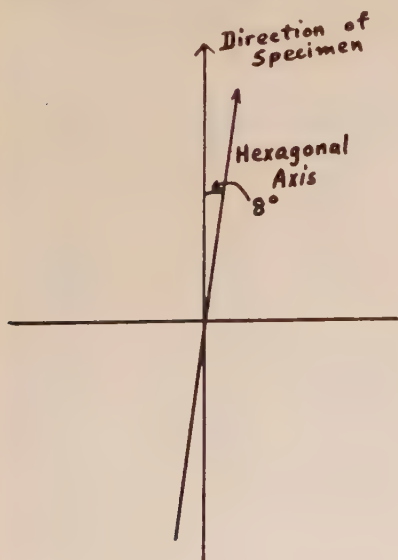


FIG. 14.—DIRECTION OF HEXAGONAL AXIS OF FIG. 11.

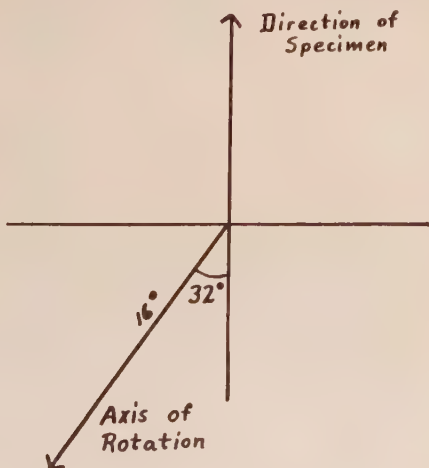


FIG. 15.—ROTATION OF PRISM OF FIG. 11.

As shown in Fig. 14, the hexagonal axis forms an angle of about 8° with respect to the long axis of the specimen. From the position of the pyra-

midal and prismatic planes, as shown by various spots, it is possible to calculate the axis of rotation and the amount of rotation of the hexagonal prism with respect to the direction of the specimen. The result is shown vectorially in Fig. 15, in which the vector points in the direction of counter-clockwise rotation. A correction for the 5° rotation of the crystal from the perpendicular direction with respect to the X-ray beam has been applied. The single rotation of the prism is therefore 16° about an axis inclined -32° relative to the axis of the specimen as shown in Fig. 15.

In the Laue pattern (Fig. 12) the specimen was in a horizontal position, as the film shows. The after-elongation thread was at the right. Although the specimen was revolved about an axis almost parallel to the X-ray beam, no rotation about an axis normal to the beam was experienced. The specimen was mounted with a piece of hard plasticine on a brass plate fixed with respect to the X-ray beam. Through a hole in the plate, the rays were allowed to strike the specimen, as shown in Fig. 13. No deformation of the plasticine was caused by the shift in position of the specimen. Therefore the angles of rotation of the prisms, as given by the experiments, may be directly compared.

TABLE 9.—*Monochromatic Pinhole Spectrogram of Single-crystal Zinc, Plastically Deformed into Elliptical Ribbon by Simple Tension*
Distance from Specimen to Film, 95 Mm.

Spot Number	Radial Distance of Spot, Mm.	Tangent of Angle between Beams	Angle between Beams, Degrees	Angle of Reflection, Degrees	Planes
1	17	0.179	10.15	5.1	
2	32	.337	18.6	9.3	$10\bar{1}0$
3	44	.463	24.8	12.4	$10\bar{1}2$
4	53	.558	29.2	14.6	$11\bar{2}0$
5	55	.580	30.1	15.0	$11\bar{2}0$
6	61	.643	32.7	16.4	
7	67	.705	35.2	17.6	$11\bar{2}2$
8	70	.737	36.4	18.2	
9	15	.158	9.0	4.5	
10	34	.358	19.7	9.8	$10\bar{1}1$
11	42	.442	23.8	11.9	$10\bar{1}2$
12	40	.421	22.8	11.4	$10\bar{1}2$
13	56	.590	30.5	15.3	$11\bar{2}0$
14	43	.452	24.3	12.2	$10\bar{1}2$
15	34	.358	19.7	9.8	$10\bar{1}1$
16	29	.305	17.8	8.9	
17	45	.474	25.4	12.7	$10\bar{1}2$
18	49	.516	27.3	13.6	$11\bar{2}0$
19	60	.632	32.3	16.2	

In this case some of the planes are seen to be distorted, from the formation of characteristic fourth-order bands, as has been previously shown in the literature.¹⁴

For the interpretation of the Laue pattern, employing as it does a beam of multiple wave lengths, some sort of projection is advisable. The gnomonic projection¹⁵ has been employed in the present analysis.

Although the distance from the specimen to the film in all of these photographs was 95 mm., the suggestion of Wyckoff has been followed and the projections have all been constructed so that the plane of pro-



FIG. 16.—GNOMONIC PROJECTION PLOT OBTAINED WITH RAY PARALLEL TO TRIGONAL AXIS.

jection is 50 mm. from the specimen. Accordingly, if the X-ray beam had traversed the specimen parallel with the trigonal axis, the gnomonic projection would have appeared as in Fig. 16, with the length of the sides being 107.1 mm. and the smaller angles 60° as shown. The gnomonic projection actually obtained is shown in Fig. 17. Considering the difficulty involved in placing the spots by estimation of the positions of maximum intensities in lines, it is thought that the points plotted agree with the indices assigned very well. The points on the projection are

¹⁴ J. Leonhardt: Die Deutung der Lauediagramme deformierter Kristalle. *Ztschr. f. Krist.* (1925) **61**, 100.

¹⁵ R. W. G. Wyckoff: The Structure of Crystals, 123. Chem. Cat. Co., Inc., 1924.

numbered in the circles to correspond with the spots as numbered on the photograph.

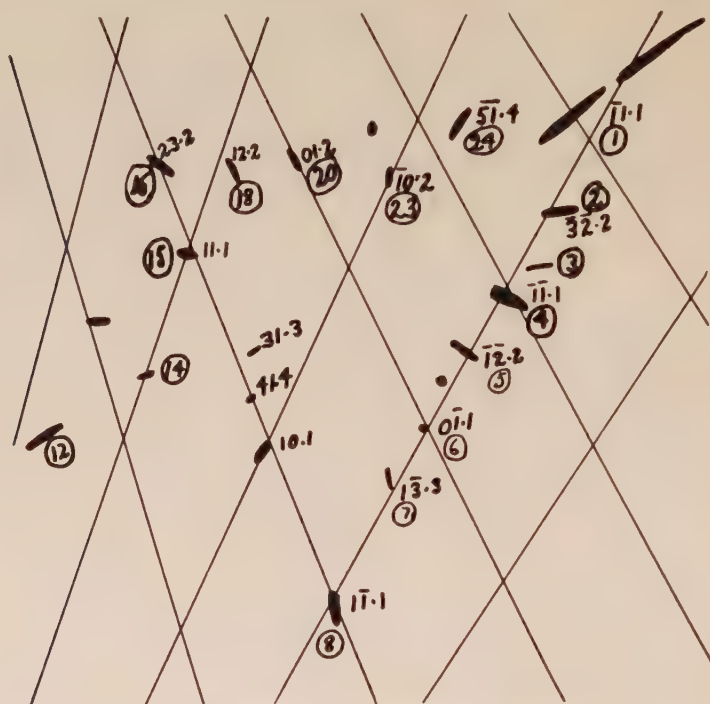


FIG. 17.—GNOMONIC PROJECTION OF FIG. 12.

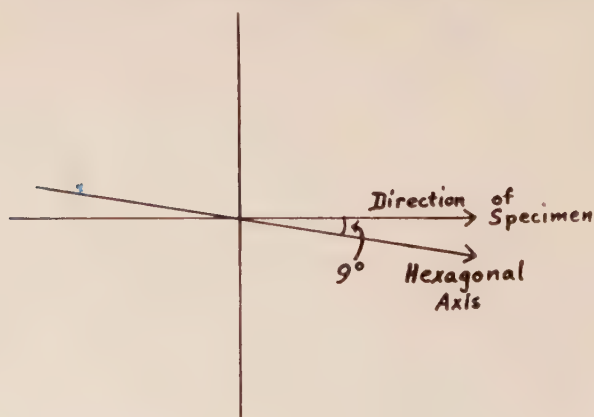


FIG. 18.—DIRECTION OF HEXAGONAL AXIS OF FIG. 12.

Since the projection of the normal of the $11\bar{2}1$ plane on the basal plane coincides with the hexagonal axis, spots 1 and 15 were used to calculate the angle between the hexagonal axis and the long axis of the

specimen. As shown in Fig. 18, this angle is 9° . The rotation of the elementary prism from a position of true parallelism between the X-ray beam and the trigonal axis is shown vectorially in Fig. 19, as a rotation of 12.5° about an axis of -14° to the axis of the specimen. The vectors have the same sense as in Fig. 15. A correction for the angle of 85° between the specimen and the X-ray beam has been applied (Fig. 13).

These results, tried out with a model of the hexagonal lattice, give a confirmation of the classical theory of the deformation of these crystals. To make such a test easier, the necessary data have been collected in Table 10. It will be noticed that the data indicate a rotation of the basal planes more into the plane of the surface of the specimen as the point of necking down is approached. At this stage of deformation,

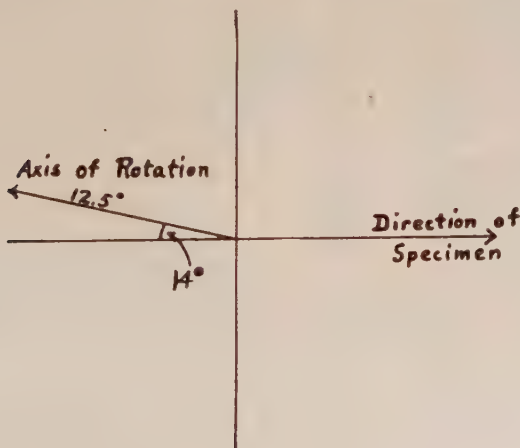


FIG. 19.—ROTATION OF PRISM OF FIG. 12.

the crystal does not show the fragmentation which would be a necessary consequence of the twinning theory.

Another interesting fact is brought out by an inspection of Fig. 12. Spot 8 represents a $1\bar{1}01$ plane, the normal of which is almost perpendicular to the longitudinal axis of the crystal. During plastic deformation, this plane has evidently been deformed very little. Spots 1 and 15 represent pyramidal planes lying in the general direction of the axis. The appearance of the bands shows that both of these planes have been warped. This is what would be expected on the basis of the classical theory for it would be impossible to produce the slipping and rotation of the basal planes, as postulated, without at the same time causing drastic changes in the atomic arrangement along the $11\bar{2}1$ direction.

One photograph was taken of the after-elongation thread, by the Laue method (Fig. 20). An attempt was made with the gnomonic projection to solve this photograph, giving the results shown in Fig. 21.

Fig. 22 shows the hexagonal axis of the crystal to be inclined 43° with respect to the wire axis. Fig. 23 shows the single rotation of the elementary prisms to be 15° about an axis inclined -15° with respect to the wire axis from the position in which the X-ray beam would be parallel to the trigonal axis. It is probable that this amount of rotation is only an approximate value which is approached by certain sections of the after-

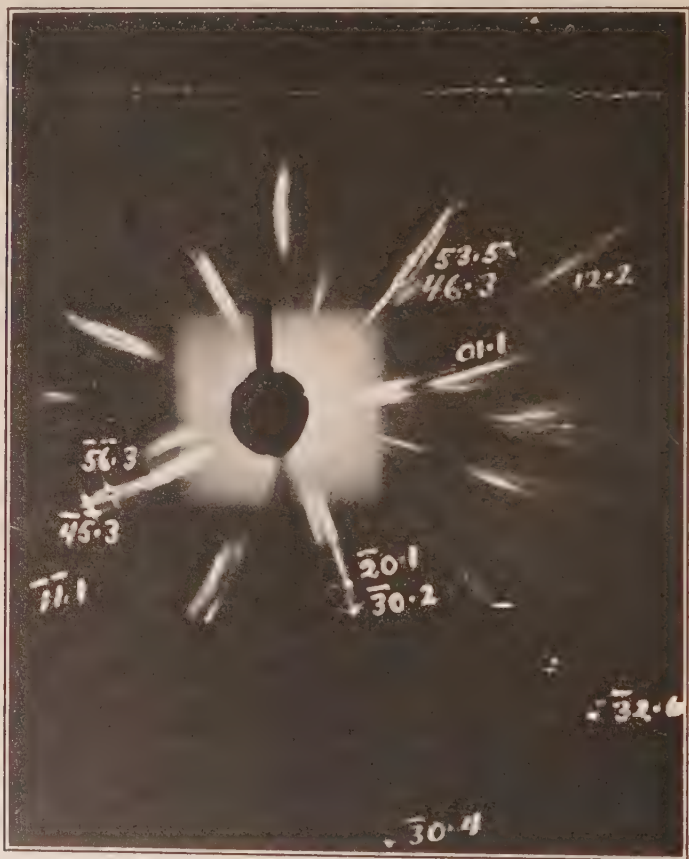


FIG. 20.—AFTER-ELONGATION THREAD OF DEFORMED ZINC SINGLE CRYSTAL.

elongation thread, since planes so severely distorted must vary in orientation from point to point.

In Fig. 18, it was shown that the hexagonal axis was inclined 9° to the axis of the crystal at a point just before the after-elongation thread. Fig. 22 shows that the angle of inclination has increased to 43° . This represents a rotation of 34° . Rough measurements on Fig. 10 with a protractor showed that the change in this angle was 30° . This difference is probably within the limit of the experimental error of the two methods

employed to get these results. The same face of the crystal was probably turned toward the source of illumination in both cases, as the zinc ribbon had a flat side which caused the crystal to assume that position.

The planes recorded in Fig. 20 are all considerably distorted, but nevertheless the tendency to retain the single-crystal formation is evident. In fact, this spectrogram is our best evidence on this point and proves conclusively that the lattice of the after-elongation thread is in a very well preserved condition. It also shows the extent of the departure

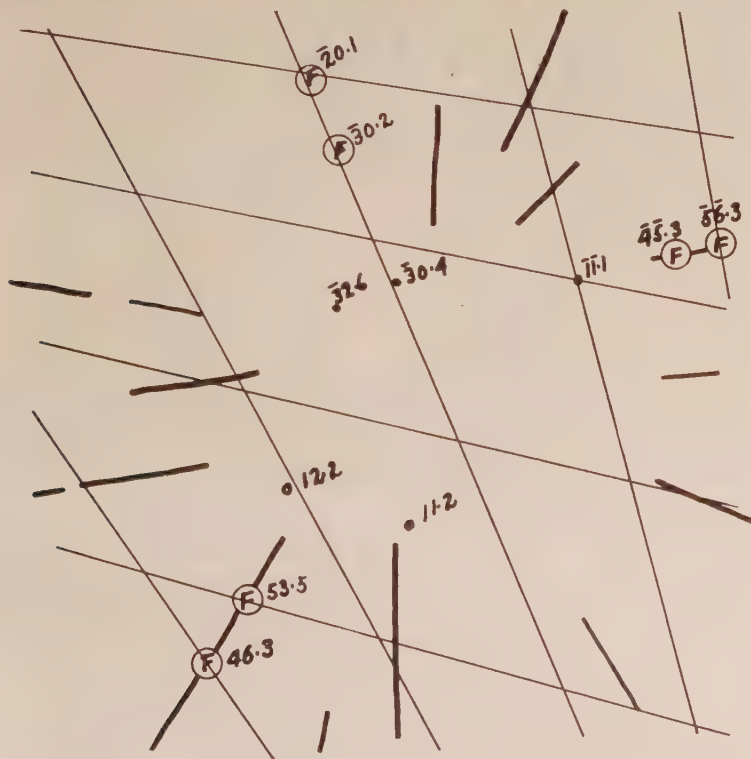


FIG. 21.—PART OF THE GNOMONIC PROJECTION OF FIG. 20.

from perfect crystallinity. If the condition approached that of random orientation, the multi-wave length X-rays used in the Laue method would produce a rather general fog instead of the well defined spots and bands. Furthermore, it is evident that this crystal has about reached the limit of deformation commensurate with the retention of its single-crystal structure. This is evident from the tendency of certain of the spots to form arcs of circles. The planes showing this effect are usually planes of fairly high index and are indicated on the gnomonic projection by F . Their distribution about the film in a fairly regular manner probably denotes a preferred orientation. Here, then, it is quite likely that

mechanical twinning in the sense of Mathewson and Phillips, or of one of the present authors,¹⁶ has occurred. The investigation of the after-elongation thread is being pursued further at the Research Laboratory.

The X-ray evidence presented here confirms the theory that tensile extension of zinc single crystals occurs by basal slip accompanied by

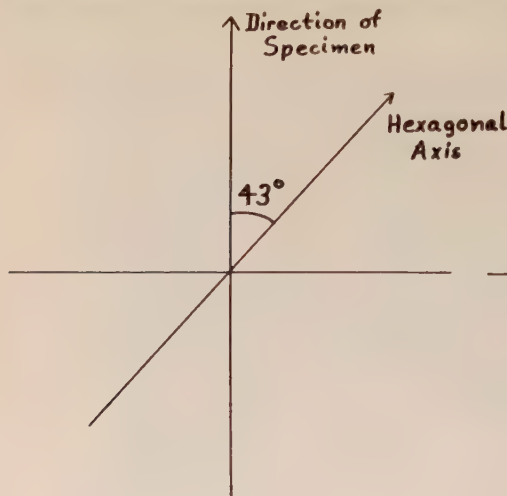


FIG. 22.—DIRECTION OF HEXAGONAL AXIS OF
FIG. 20.



FIG. 23.—ROTATION OF PRISM
OF FIG. 20.

tilting and rotation. This movement produces warping in other lattice planes in the line of slippage. There is no evidence of twinning or of fragmentation which produces random orientation until after very considerable extension of the crystal has occurred.

STUDY OF THE CLEAVAGE FACES OF ZINC CRYSTALS

The last stage of the work consisted in taking X-ray patterns of the cleavage faces of fractured single-crystal specimens of zinc. One of the samples was the one supplied by Professor Mathewson and was about 0.5 in. wide by 20 mils thick. It was pulled apart by clamping one end in a vise and pulling on the other end with a pair of pliers. The second specimen was prepared in the laboratory in the way used for our other crystals. It was broken by two persons gripping the ends in pliers and pulling until fracture occurred. In both cases typical cleavages were obtained. X-ray patterns were obtained of these cleavage faces by means of a grazing beam, as is shown in Fig. 24. The specimen

¹⁶ See the 1927 A. I. M. E. papers referred to above. (The latter as shown in Fig. 9 of the discussion.)

was mounted so that the cleavage surface formed as nearly as possible an angle of 17° or 8° respectively with respect to the incident beam. This position was used because it is the correct one for basal reflection and furnishes a test of the presence of basal planes in the cleavage surface. This, it may be recalled, would confirm the correctness of the twinning hypothesis. The cleavage surface, however, was not a true plane and this allowed part of the surface to come into proper relationship with the X-ray beam to produce reflection from the prismatic planes, should they lie in the surface. If either reflection were absent, we would have evidence that that plane did not lie in the plane of the fracture.

The patterns obtained are shown in Figs. 25 and 26, which represent the results on Professor Mathewson's crystal and on our own, respectively. The photographs of the cleavage faces are compared, in each case, with the pattern from zinc powder, in order that a comparison of the

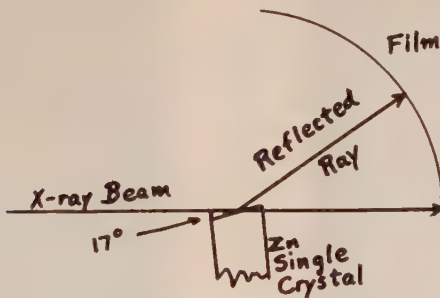


FIG. 24.—EXAMINATION OF CLEAVAGE SURFACE OF ZINC SINGLE CRYSTAL.

intensities of the lines with the theoretical intensities may be more easily obtained. Any deviation of the observed intensities from the values furnished by random orientation indicates a preferred orientation. That such preferred orientations were obtained is at once evident from an inspection of the figures, or of Tables 11 and 12, in which the readings of the films are tabulated. These intensities are recorded in arbitrary units, using the intensity of the brightest line as 10. The intensities of the other lines are then estimated by comparison with this line as a standard. Many more lines appear on the films than are recorded in the tables, but only those lines which appear on the film in Fig. 25 with sufficient strength for our present purposes have been used. These reflections are commonly those from the basal and prismatic planes. That these lines are not complete in the fracture spectrograms is not significant, since the cleavage surfaces experimented with were so small that the lines must necessarily be short.

The surface markings on Professor Mathewson's crystal were similar to those described in Mathewson and Phillips' paper. The first two attempts to fracture this crystal resulted in tears and it was not until

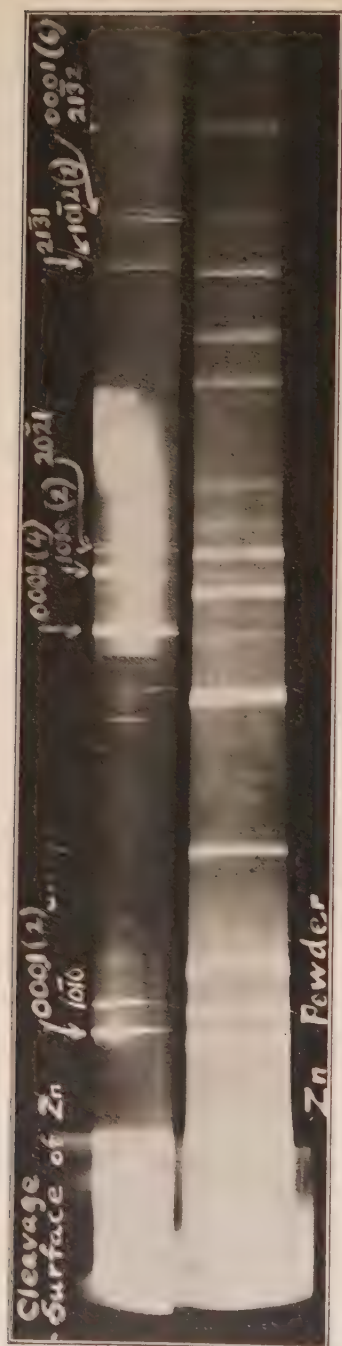


FIG. 25.—CLEAVAGE SURFACE OF THICK ZINC SINGLE CRYSTAL.



FIG. 26.—CLEAVAGE SURFACE OF SLENDER ZINC SINGLE CRYSTAL.

the third attempt that a clearly defined surface was obtained. This indicates that twisting and bending, as well as tension, have acted on this crystal, as a rather complicated stress system. For example, on the inside of a bend, there is compression, and on the outside, there is tension. Here, then, twinning is to be expected and its presence is shown by lines from sets of planes which cannot be reconciled to any orientation of a single crystal. Table 11 gives some evidence of this effect, inasmuch as the reflections from the 0001 (4) and the $10\bar{1}0$, (2) planes are especially intense. Furthermore, in accordance with the manner in which the crystal was mounted, these planes lie in, or very nearly in, the cleavage surface. An inspection of the model of the hexagonal lattice shows that it is impossible to secure reflections simultaneously from the basal plane and the prismatic plane of a (virgin) single crystal. Therefore, in this case, it seems logical to assume twinning to account for the reflections shown.

The strains which produce bending in the crystal can be diminished or eliminated altogether by (1) eliminating stresses which have components in directions perpendicular to the direction of tension, or (2) by decreasing the cross-section of the crystal, leaving the length the same. The conditions under which these cleavages were produced were the same regarding (1) in so far as the technique would permit. Any difference noted in the spectrograms of the two crystals is in all probability due to the fact that the crystals produced in this laboratory are much smaller in cross-sectional area than those produced by Professor Mathewson. Bending moments are consequently much reduced and the cleavage surface of a small crystal represents more nearly a condition obtained with simple tension.

An inspection of Fig. 26 and Table 12 shows that the spectrogram of the fracture of the small crystal grown in this laboratory is much simpler than that of the larger crystal. The only prominent reflection is that of the prismatic plane, which shows that it is almost exclusively the plane which lies in the plane of the fracture. The presence of many lines of low intensity in Fig. 25, of the larger crystal, makes it seem very probable that the complex forces exerted on the atoms of such a crystal have produced some fragmentation, so that the cleavage surface is made up of a large crystal interspersed with a few smaller ones approaching random orientation. The very simple nature of the spectrogram of the smaller crystal shows such effects to be negligible. It would hardly be expected that Laue photographs of Professor Mathewson's crystals, after they have been subjected to plastic deformation in the manner described, would show such a persistence of the single-crystal condition as is shown in Figs. 12 and 20. Such photographs would be very interesting.

Finally, it may be said that when zinc crystals are subjected either to very severe elongation or to stresses having components in several direc-

TABLE 10.—*Analysis of Positions of Elementary Prisms in Two Positions of Plastically Deformed Ribbon of Zinc Single Crystal*

	Point Far from Point of Neck- ing Down, Degrees	Point Near Point of Necking Down, Degrees
Angle between hexagonal axis and direction of specimen.....	8	9
Amount of rotation of prisms from parallelism with trigonal axis and X-ray beam.....	16	12.5
Angle between axis of rotation and direction of specimen.....	-32	-14

TABLE 11.—*Spectrogram of Cleavage Surface of Zinc Crystal Grown by Dr. Mathewson*

Interplanar Distance, Angstrom Units	Plane	Intensity of Reflection		Angle between Plane and Beam, Degrees
		Zinc Filings Control	Zinc Fracture	
2.47	0001 (2)	9	10	8.3
2.31	10 $\bar{1}0$	9	7	8.9
1.237	0001 (4)	4	10	16.8
1.155	10 $\bar{1}0$ (2)	2	9	18.0
1.124	20 $\bar{2}1$	8	6	18.4
0.860	21 $\bar{3}1$	8	6	24.6
0.845	10 $\bar{1}2$ (2)	1	5	25.0
0.824	0001 (6)	4	5	25.6
	21 $\bar{3}2$		5	
0.772	21 $\bar{3}3$	5	3	27.4
	10 $\bar{1}0$ (3)			

TABLE 12.—*Spectrogram of Cleavage Surface of Zinc Crystal Grown from Melt*

Interplanar Distance, Angstrom Units	Plane	Intensity of Reflection		Angle between Plane and Beam, Degrees
		Zinc Filings Control	Zinc Fracture	
2.47	0001 (2)	9	1	8.3
2.31	10 $\bar{1}0$	9	10	8.9
1.237	0001 (4)	4	0	16.8
1.155	10 $\bar{1}0$ (2)	2	0	18.0
1.124	20 $\bar{2}1$	8	1	18.4
0.860	21 $\bar{3}1$	6	0	24.6
0.845	10 $\bar{1}2$ (2)	1	0	25.0
0.824	0001 (6)	4	0	25.6
	21 $\bar{3}2$			
0.772	21 $\bar{3}3$	5	0	27.4
	10 $\bar{1}0$ (3)			

tions, twinning and fragmentation occur. But zinc crystals subjected to unidirectional stress, persist in the single-crystal condition even though the elongation may reach large amounts. In this case the twinning hypothesis is untenable and the classical theory must be accepted.

SUMMARY

1. Cold rolling of polycrystalline zinc strip causes rearrangement of the zinc crystals in accordance with the classical theory of plastic deformation. There is no evidence of twinning.

2. Extension of slender zinc single-crystal specimens causes rearrangement of the basal planes in accordance with the classical theory. The single-crystal structure tends to be preserved.

3. The formation of the after-elongation thread is accompanied by severe lattice deformation which promotes twinning and fragmentation. The single-crystal structure, however, appears very permanent.

4. The fracture of a thick zinc crystal occurs as depicted by the Mathewson-Phillips hypothesis. Twinning is present. The fracture of slender zinc crystals under simple tension is prismatic. Twinning is absent.

DISCUSSION

L. W. MCKEEHAN, New Haven, Conn.—A trivial correction should be made to the quotation of the axial ratio of zinc from Wyckoff. His figures give the value 1.862, and these figures are taken from the work of Peirce, Anderson and Van Dyck, which is also quoted here. I have pointed out in previous discussions that the figure 1.86 is only an approximation.

The argument beginning on page 243 in regard to the angles that planes in the original and twinned crystals make with the X-ray beam and with the surface is, I think, hard for most people to follow. It was very difficult for me, and I had to reinforce my notion of what the authors meant by drawing a diagram (Fig. 27). The X-ray beam appears in the center of the picture, so that the distribution of spots on the diagram that is obtained will be in a plane parallel to the plane of the picture. If a basal plane has its pole B at the right in position to reflect, that is, if the angle XB is 81.1° , the spot will appear farther out on the right. If twinning on the Mathewson-Phillips theory takes place, the new basal plane will be at 94° (nearly) from this basal plane, and if it also is to reflect, its pole must lie on the same broken circle on which B lies. The circle of 94° radius about B appears on this diagram as an almost straight line near the center of the figure. All the twinned basal planes will have their poles on this line, no matter what the position of the original crystal with respect to its trigonal axis B , and the pole of the one twinned basal plane that reflects is marked B' . These two crystals have a common axis, one of the three axes of the hexagonal set. It is, however, a digonal axis, and is marked D and D' at the same point near the center of the diagram.

The authors make an error, I believe, in stating that the angle between X and D is 8.3° ; examination of the diagram, or a calculation, will make it nearer 12° . They also say that the structure can be turned in either direction about the normal to the twinned basal plane, i. e., about B' , without changing XD . This, I think you will see from the diagram, cannot be true.

There is a trivial error committed in calling the axis D the "hexagonal" axis. It is one of the three axes used in the hexagonal system, but none of them, in this case, is an axis of hexagonal symmetry. The trigonal axis is the one perpendicular to the basal planes and there are two digonal axes at 120° to each other in the basal plane. These three are customarily used for reference, the third digonal axis in the basal plane being neglected.

The argument in regard to the pyramidal planes of the form $\{11\bar{2}2\}$ seems also to be out of line with the evidence. If we mark the positions of the normals to these pyramidal planes in the diagram, they lie on a circle at a distance of 61.8° from the point B . These points are marked C . They not only fall on this circle but at definite positions on it. In the twin crystal the corresponding positions are marked

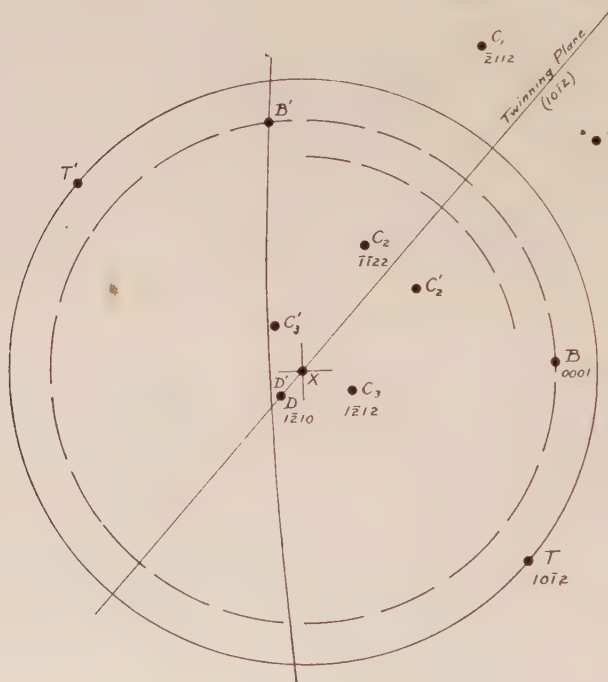


FIG. 27.

C' , and inspection shows that no one of these pyramidal planes (these are all there are) is in position to reflect the X-rays. To reflect X-rays the poles of such planes must lie on the broken arc in the upper right of the figure. This arc is of somewhat smaller radius than in the case of basal planes. So I conclude that reflection in both pyramidal planes and basal planes in the twin would be impossible.

In Table 1, and later throughout the paper, there is a mistake in the ascription of one possible reflection to the third-order reflection from the basal planes. The first, third, and all odd orders of reflection from these planes are extinguished. The proper entry in each case should be 1013. The corresponding angle, which should appear in the second column of Table 1, is 35.6° , not zero. The $11\bar{2}0$ plane makes with the basal plane an angle of 90° , of course. There is one pyramidal plane of the second kind, $11\bar{2}1$, omitted from the table.

The argument immediately below Table 1, I need not criticize in detail, but there is a mistake in the angles; 78.5° and 127.5° should be, respectively, 74.5° and 131.1° .

The use of the term "fourth-order bands" in describing the streaky appearance obtained when the crystal planes are much bent and distorted is, I think, unfortunate, because we are also dealing with first, second, third and fourth-order reflections from planes of different sorts, and the term might just as well have been translated as "curves of the fourth degree," keeping the term "order" for the ordinary order of X-ray reflection.

Figs. 3 to 8 do, of course, give some evidence for preferred orientation of the crystal assemblies to which they belong, but the reproductions, at least, are not sufficiently definite to make sure of the preferred orientation, even when supplemented by the numbers in the tables. There is some degree of orientation, but just what it is has not been completely analyzed.

The difference in the two sides of Fig. 8 favor a view held by Schmid and Wasserman with regard to the drawing and rolling of copper, and also some results of Prof. G. L. Clark's on rolled sheet. The two halves of the sheet, corresponding to the halves of the pattern in the direction of rolling and in the opposite direction are not necessarily the same. This is probably due to the fact that the stresses at the point where the reduction in thickness is taking place are not symmetrical about the line of contact of the rolls.

The monochromatic photograph, so-called, shown in Fig. 11 and analyzed farther along in the paper, is not a monochromatic photograph at all, and this can be proved directly from the appearance of the photograph itself. It is a Laue photograph. Table 9 shows the same thing, because some of the spots are nearer the center than is possible if they are due to any monochromatic radiation from molybdenum, and so much nearer that there must be waves present with wave lengths of about 0.4 \AA -strom units. This shows a range of wave lengths of practically an octave, even if there are no longer waves than those supposed to constitute the whole radiation in the beam. What is taken for monochromatic light is far from being so. The same thing is seen in Table 3, where the minimum angle is 3.6° . The indexing of the spots on Fig. 11 has been in error because of the assumption that monochromatic light was being used. This is evident in another way.

If we look at the spots which have the indices $11\bar{2}0$ we still find three of them. These are prism planes of the second kind and there are just three such planes in the whole crystal. The three spots due to these planes must lie (this being a single crystal) on an ellipse—nearly a circle—passing through the center. These three spots here form a triangle which includes the center, so no such ellipse can be found. The indices are therefore wrong. Another plane of the same zone is $10\bar{1}0$ (spot 2), and that also cannot lie as it should on the same ellipse with the three just mentioned. If it had been recognized as a Laue photograph, of course, much higher indices would have been ascribed to many of the spots.

When we come to the Laue photograph (the admitted Laue photograph) which is projected in Fig. 17, the projection is, I think, consistent with the data except for one thing. The spot at the upper right-hand corner, marked $\bar{1}1.1$ would appear, if it had these indices, at the intersection just above spot 20 at the top of the figure. The indices for the position marked would be $2\bar{1}.1$.

The Laue photograph, however, has not been checked; at least if it has been the evidence has not been given. The only way a Laue photograph can be made of real value is to ascribe a wave length to each of its spots, calculated, of course, from the position of the spot and from the spacing of the planes to which it has been ascribed. Having thus ascribed a wave length to each of the spots on the photograph, find out whether that wave length is probably present in the original X-ray beam. If every spot satisfies this test the Laue photograph *may have been* correctly marked.

In Fig. 21 there have been two mistakes in marking indices. The spot marked 53.5 would be marked 58.5 according to its position. The spot 56.3 would be 46.3. As long as indices are being ascribed, I am surprised that the authors did not give the very simple indices 01.1 and 01.1 to the two streaks which appear right and left on the third line from the top of the diagram. The asterism here shown is quite characteristic of very much deformed metal crystals.

I wish to make a major objection to the technique described in the study of cleavage planes. The crystals were set in one position and the reflections taken. That is hardly fair because if the position is not exactly right the relative intensity of reflection from the different sorts of plane which may lie near the surface is much affected by any error in setting. What should be done in such a study is to rotate the specimen through an angle which includes the angles under investigation, both of them. In this case the crystals should have been rotated so that the angle of reflection ran from 5° to 15° . The intensity of the lines of such a diagram could properly be compared to tell which of the two planes in question lay approximately parallel to the surface.

I have assumed throughout this discussion that molybdenum K-radiation was used. There is no statement to that effect and it would be better if there were.

C. H. MATHEWSON, New Haven, Conn., (written discussion).—This paper sets the so-called classical theory of deformation as described by Polanyi and his associates in opposition to a so-called twinning theory derived from Mathewson and Phillips and seeks to prove that the latter does not apply in rolling polycrystalline zinc or in stretching small single crystals.

The classical theory resulted from a brilliant set of experiments in which basal slip was recognized as the predominating cause of ductility in single-crystal wires and by analogy in crystal aggregates. Mathewson and Phillips demonstrated the nature of twinning in zinc and pointed out its significance in the general process of deformation.¹⁷ The two theories, if we use this term to designate the two kinds of crystal movement or alteration recognized and rather elaborately described in these papers, constitute the tools thus far made available for studying any particular deformational process in zinc. In my opinion they are mutually compatible and support one another in furnishing a complete and plausible explanation of commonplace but complicated deformational processes such as the progressive change by current rolling-mill methods from coarse-grained cast zinc of substantially random orientation to fine-grained ductile strip in which pronounced selective orientation is apparent.

Twinning cannot of itself elongate or otherwise change the shape of a crystal to any considerable extent. This was clearly recognized in the Mathewson and Phillips paper.¹⁸ Twinning produces alteration in an unfavorably orientated crystal, so that basal slip can occur and it has been amply shown that during such basal slip—in the rolling process, for example—strongly preferred orientations are set up.

The polycrystalline strip used by the authors had been "rendered ductile by appropriate heat and mechanical treatments." The details of rolling are not given but, as far as I can ascertain, the criterion of ductility in rolled zinc strip is preferred orientation of the sort that will favor further extension by basal slip when the same rolling process is continued.

Twinning in the breaking down or roughing stages of the rolling process does not require the X-ray for identification. It is always evident on simple microscopic examination. If the twinned relationship cannot be recognized in the finished strip,

¹⁷ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. of Metals Div., A. I. M. E.* (1927) 143.

¹⁸ *Op. cit.*, 178.

as maintained by Wilson and Hoyt, it must have been obliterated by subsequent basal slip and rotation in the Polanyi sense.

It is, however, not extravagant to suppose that the authors might have been unable to detect twinning in this strip because their method was based upon the observation of random orientation or fourfold symmetry in the pinhole patterns, denoting far-reaching regularity and perfection of the twinning process; whereas actual twinning under the rolling process would only occur on certain favored planes in certain crystals unfavorably orientated for primary basal slip, thus confusing or degrading the symmetry relationships.

In this connection T. E. Kihlgren¹⁹ in an attempt to determine the orientation of zinc crystals by measuring the angles between twin bands, previously produced by bending in all possible directions in a vise, was never able to develop all of the six possible sets of bands. Two or three sets could be obtained with ease. Four crystals out of a large group gave four sets and one exceptional crystal gave five sets. The quoted remarks of the writer on page 250, specifying the number of orientations possible by multiple twinning within a single crystal, are not to be construed as direct evidence in the present case since they refer only to geometrical possibilities. We have thus far been able to detect with certainty, in large crystals strained by rolling, only three superimposed (multiple internal) twinings, representing an insignificant fraction of the total number of orientations which would result from participation of all potential twinning planes.

Wilson and Hoyt obtained their 4-mil strip by lengthening the parent 13-mil strip without changing the direction of rolling. No rolling details are given but the spectrograms clearly indicate a coarsening of the grain which denotes hot-rolling in the sense that sufficient heat is developed during rolling, when the process is continuous and the pinches heavy, to keep the metal soft and even develop a moderately coarse grain. This is the ordinary method of finishing soft zinc strip. It permits slip to continue along the favorably orientated basal planes. In my opinion, twinning would be largely confined to the first cold work in the rolls before the metal had opportunity to warm up internally. The relative amounts of twinning and slip in these early stages would depend on the purity of the metal, the temperature and the orientation of the crystals. Much more twinning would be produced by cross-rolling, as the crystals at the start would not be favorably orientated for slip in this direction. The true conditions in any case could only be determined by painstaking study of the process at all stages. The broad statement by the authors that there is no evidence of twinning in the cold rolling of polycrystalline zinc strip is unwarranted because observations were made only at the beginning and end of a particular cold-rolling process applied to a particular strip in a manner calculated to produce slip without much twinning. Abundant evidence of twinning is on record in the photomicrographs on file at Palmerton, representing the structure of rolled zinc in a variety of temper conditions and in various stages of both the cold or hot-working processes.

Wilson and Hoyt appear to have made a thorough examination of the slender single-crystal ribbon which disposes of my proposal that bending of the basal lamellas during slip in the Polanyi sense ought to produce twinning. On the other hand, the main point of my original discussion relative to structural changes during extension of the ribbon, namely, that twinning and secondary basal slip accounts for an after-elongation after exhaustion of the primary basal slip, seems unimpaired, since the authors conclude that twinning has occurred in this part of the ribbon. The phraseology on page 263 seems to indicate that the so-called "twinning theory" would require a condition of random orientation in this after-elongation thread. This is quite different from my proposal that twinning serves to reorient the basal planes in a

¹⁹ Master of Science Report, Yale University, 1927.

perfectly definite manner so as to permit slip of the prismatic form observed by Polanyi in the after-elongation thread. The authors' continually emphasized point that the lattice of the after-elongation thread is in a "well preserved condition" meets perfectly the requirements of the twinning theory as I have it in mind.

Finally, the authors deal with cleavage faces, both of the slender crystals used by Hoyt in the earlier work and the more massive crystals used by Mathewson and Phillips, but their actual observations seem unfortunately to be confined to two cleavages, one in each kind of crystal, and the results in my opinion are not conclusive. The authors believe that the slender crystal cleavage is prismatic in spite of the fact that there is a certain amount of basal reflection with the crystal mounted so as to reflect from basal planes should they lie parallel to the surface. The twinning theory calls for a striated combination of basal and other (perhaps prismatic) fracture elements which might give rise to quite a variety of X-ray effects depending on the widths of the striae and their positions relative to the X-ray beam.

W. M. PEIRCE, Palmerton, Pa.—I agree thoroughly with Dr. Hoyt that the X-ray evidence should be critically examined in the light of the microscopic evidence. We have been working for a good many years at the New Jersey Zinc Co. Laboratory on rolled zinc, studying its structure microscopically, and we have been using the presence of twinning as a means for detecting cold rolling in rolled strip.

(Written discussion).—The first statement in the authors' summary is that there is no evidence of twinning in the cold rolling of polycrystalline strip zinc.

Cold rolling should be used, to designate rolling under such conditions that the internal temperature of the metal does not exceed the recrystallization temperature. Some care is required to meet these conditions in rolling pure zinc.

Twinning can be readily detected in the microstructure of zinc, in fact it is one of the distinguishing differences between hot-rolled strip and strip which has undergone a moderate degree of cold rolling. Thus it appeared of interest to the writer to present the results of the following simple experiment carried out by J. L. Rodda in our laboratory.

A piece of 0.024-in. hot-rolled Horsehead strip was given a 30-sec. anneal at 250° C., which is sufficient to remove twins resulting from accidental deformation during handling without altering the general type of structure or appreciably changing the physical properties.

Fig. 28 shows the original slightly twinned strip and Fig. 29 the unstrained structure after annealing. Fig. 30 shows extensive twinning after a 4 per cent. reduction in one pass. Fig. 31 shows the structure resulting from 75 per cent. reduction carried out in three passes. The center portion of the field has completely recrystallized on account of the heat generated in the rolling, in spite of the fact that the rolls were cold and the strip thin. The edge of the field has not completely recrystallized but shows patches of a strained structure which we attribute to the development of a twinned structure to a point where the original crystals and the twinned fragments are too small to resolve.

The direct microscopic evidence of twinning seems to be difficult to reconcile with the first conclusion stated by the authors in this paper.

A. ST. JOHN, New York, N. Y.—I noticed that in one of the slides in the presentation of this paper, I think it was on the 4-mil piece (Fig. 6), there is a peculiar symmetry indicated in the spots as they are arranged, not on the surface but in the area near the center. I observed this repeatedly in work I have been doing recently on the application of the pinhole method, and while I have not carried out the analysis of it to any extent, I think some reference to it in the literature has been made. I believe a careful consideration of the meaning of those spots will give us a considerable amount of information.

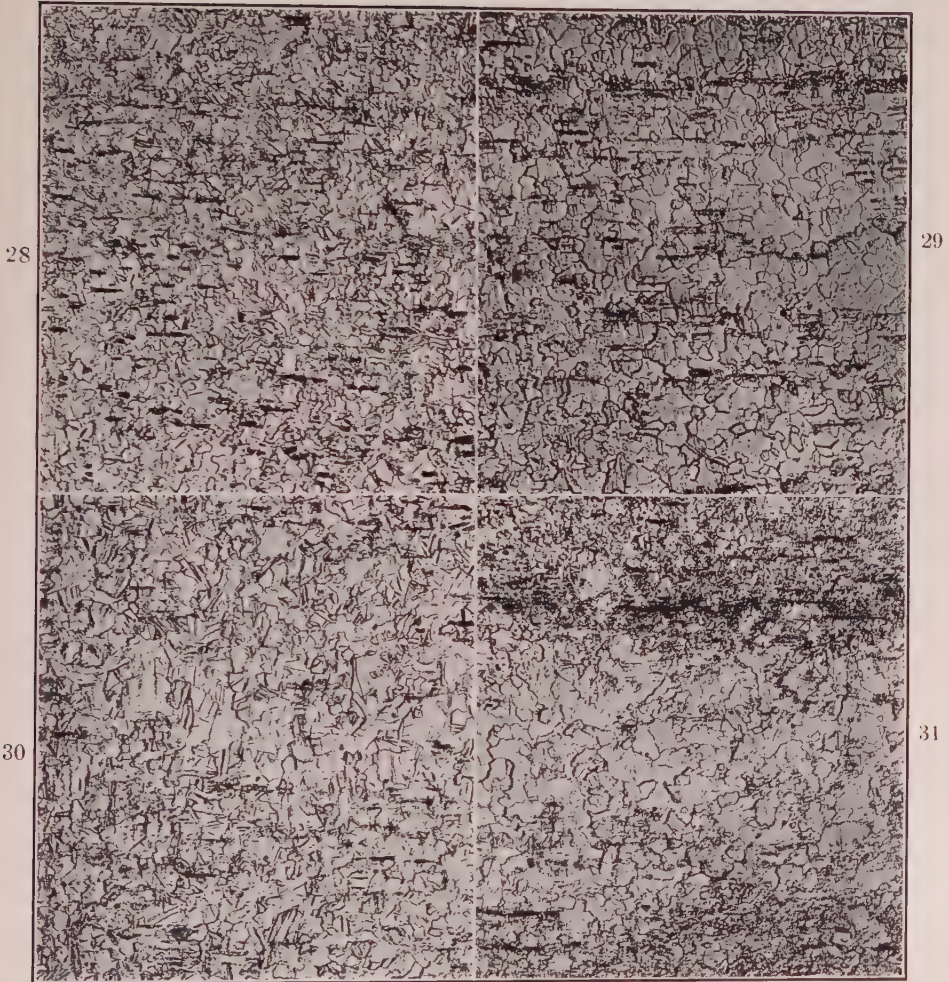


FIG. 28.—HOT-ROLLED HORSEHEAD SHOWING SLIGHT TWINNING. $\times 100$.

FIG. 29.—SAME AS FIG. 28, ANNEALED 30 SEC. AT 250° C. NO TWINNING. $\times 100$.

FIG. 30.—SAME AS FIG. 29, REDUCED 4 PER CENT. IN ONE COLD PASS. TWINNING GENERAL. $\times 100$.

FIG. 31.—SAME AS FIG. 29, REDUCED 75 PER CENT. IN THREE PASSES ON COLD ROLLS. PARTLY RECRYSTALLIZED. $\times 100$.

On the left-hand side, the spots are horizontal, whereas down through the left bottom they are coming off at various angles. On a good film, decided symmetry aspects can be seen there, almost like the magnetic field diagrams when iron filings are spread over a magnet or a group of magnets.

It is, I believe, because the individual crystals are arranged at a particular angle about the beam and consequently are giving a distorted, twisted reflection of the beam and a twisted image of the focused part. Certain diagrammatical difficulties, which I prefer to leave to Mr. McKeehan, come up with regard to the analysis of that, but I found a consideration of those conditions, entirely apart from what is going on around here, can give a very considerable amount of evidence concerning the orientation in the material.

Also on that account, it is very desirable to use not monochromatic radiation but radiation containing all the wave lengths and consider very decidedly what is happening down in this region where there can be none of the molybdenum characteristic radiation in evidence.

L. W. MCKEEHAN.—That subject was completely discussed by Dr. R. M. Bozorth,²⁰ who corrected some earlier misapprehensions of mine. It has nothing to do with the distortion of crystals or with preferred orientation.

S. L. HOYT.—This is simply a partial reply to Professor Mathewson's comments and somewhat to Mr. Peirce's comments. Mr. Wilson and I do not take the position at all that twinning does not occur in zinc. We recognize that twinning does occur in zinc. I am afraid that after listening to the discussion one will get the idea that there is some controversy on that point.

Our point of view is more that the plastic deformation, for instance, in a zinc strip occurs largely by slip along basal planes, very much according to the theory of Mark, Polanyi and Schmid, as the slipping occurs in aluminum, and so forth.

We are willing to admit that it is accompanied by twinning, but we do not feel that the twinning is responsible for any major portion of the deformation, that it is to be regarded more as a subsidiary effect, one which if eliminated completely would not materially alter the aspects of the plastic deformation of zinc. I am simply advancing that as our viewpoint and that would seem to be a very logical conclusion from the work which we have done.

(Written discussion).—With Professor Mathewson's conclusions, which he draws from his work on zinc strip and coarse zinc crystals, I am in agreement, but this situation is best to be understood in the light of his comment that the two views are mutually compatible. I had originally understood him to mean that a strain applied to our zinc strip in a transverse direction would at once produce twinning of these unfavorably oriented basal planes, and permit further slip, or in other words, that the strip should be ductile in a transverse direction immediately after rolling. Now it is apparent that this is far from his thoughts, and that it would be necessary to roll the strip transversely, to shift the unfavorably oriented basal planes into favorable orientations, before the strip would have "transverse" ductility. Professor Mathewson emphasizes the mechanism of producing ductility, while we stress the ductility itself.

His final two points deal with crystals which he has not had under direct observation, at least as far as I can infer from his discussion. I can say only that I consider them to be sufficiently treated in the paper and in the literature, and that the conclusions drawn seem to me to be the logical ones. Possibly we do not know all we should know about the movements involved, and in the light of Professor Mathewson's

²⁰ R. M. Bozorth: *Jnl. Optical Soc. Am.*, (1924) **9**, 123-127.

discussion, we should certainly know more about possible twinning movements in the slender zinc crystals. Our observations lead us to conclude that after-elongation is due to a shift of the slip movement from the basal planes to one set of prismatic planes, and our evidence is compatible with such a picture. In the literature known to me, Professor Mathewson stands alone in his picture of this movement and the importance of this work to the general theory of plastic deformation would warrant a thorough study on his part, let me point out, of these particular crystals. After all, the question is what actually occurs. From the admirable work which has been done in his laboratory, no one is better qualified than Professor Mathewson to make such a study.

From the nature of Mr. Peirce's discussion I can see that he assumes that we consider our summary to be conclusions which we would apply to cold-rolling zinc in general. What we intended to summarize there was simply our own findings in the limited investigation which we reported. My thanks are due to Mr. Peirce for enabling me to make this clear, and for supplying the information on the structure of rolled zinc. I understand the position of Mr. Peirce to be that the importance of twinning here is to produce many favorable orientations of the basal planes during the first pass, and that later deformation comes from slip along these planes. Dr. Wilson and I do not feel that our work refutes this idea; in fact, from what we now know we are perfectly willing to accept it.

T. A. WILSON (written discussion).—Dr. McKeehan is correct in his assumption that Mo K radiation was used throughout in this work whenever monochromatic radiation is specified. The source of the rays was a water-cooled Coolidge tube with a molybdenum target operating under 30 kv. potential and a current of 23 ma. For securing sensibly monochromatic radiation, the regulation zirconia filters were used. Results which have been obtained in more recent work here indicate that some of the spots produced by the shorter wave lengths in the beam when they penetrate zinc specimens similar to ours may show with fairly high intensity provided they are not too far removed from the undeviated beam impression. Inspection of Fig. 11 shows that a large proportion of the impressions to which indices are assigned are strong reflections.

Wilson and Hoyt felt that in working with such a strongly deformed crystal as that shown in these figures (Figs. 11 and 21) an average orientation was all that could be obtained. Therefore the orientations given in the article for the different regions of the single-crystal specimen are averages of closely allied orientations calculated from a large number of spots in the respective photographs. The spots chosen for this purpose were the spots of large intensity. This will explain why the inconsistencies pointed out by Dr. McKeehan did not appear with more definiteness in the deciphering of these photographs.

Reading photographs composed of band reflections such as these always presents much difficulty. It was judged impossible to select any exact spot in any band as representing a well defined plane reflection, although the spot which was judged of maximum intensity was selected as nearly as possible. This will account for a difference of opinion as to the indices of some of the planes, and for the omission of indices on the long spots of Fig. 21, which Dr. McKeehan would designate as 01.1 and 01.1.

Wilson and Hoyt in employing the terms "hexagonal axis" and "four-order bands" in the sense in which they are used in this article were simply following a rather general custom in this field. It must be admitted that there is a chance of confusion in their use, however, and the terms recommended by Dr. McKeehan are desirable as well as correct.

The discussion centering around the conclusions derived from Fig. 1 shows a misunderstanding of the reasoning there employed. It was hoped that this reasoning

might be made more understandable by the omission of projections. Apparently the opposite result was obtained.

I have taken the liberty of reconstructing Dr. McKeehan's stereographic projection (Fig. 32), simplifying it somewhat for this present discussion by omitting the spots C_2' and C_3 , which will not be considered. The spots B' , D or D' , X and C_2 have the same significance as on the original projection. Since it has been proved previously, by means of the projection, that there is a position of the twinned crystal

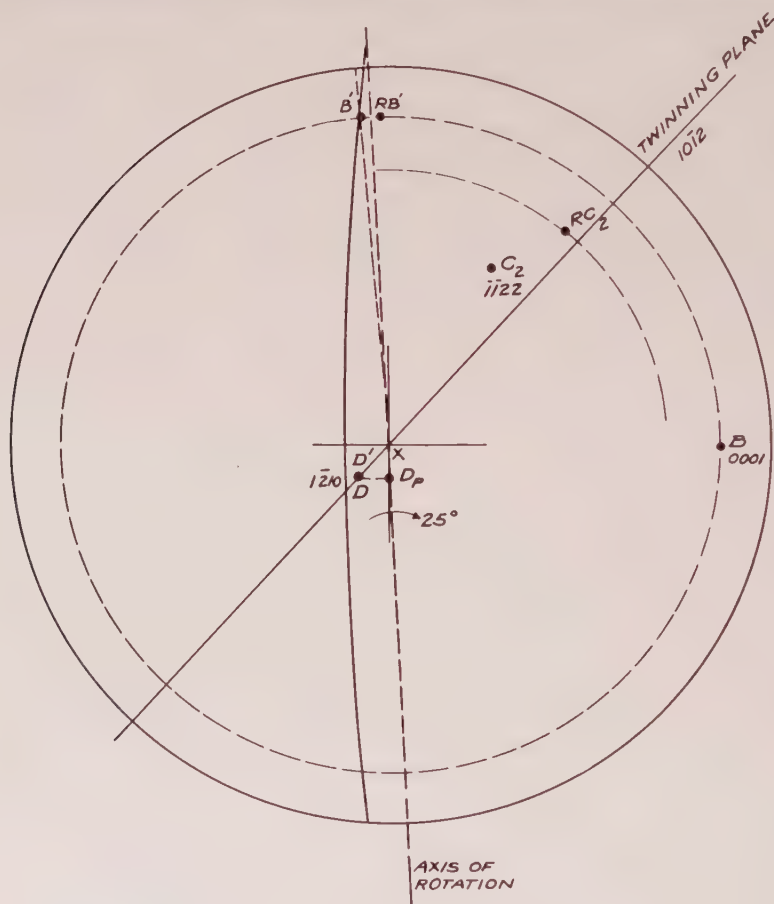


FIG. 32.

which will allow X-ray reflection from the basal planes of both the original crystal and the twin, nothing more will be said about this case, except a brief reference to the angle XD which is mentioned in the discussion. On the present construction, this angle seems to come closer to 13° than 12° . But the projection of this angle on the great circle through B' and X is the angle XD_m , which is approximately 8.3° , the angle which must exist between the basal plane and the X-ray beam before basal reflection can occur.

It remains to be proved by means of the stereographic projection that there is a position of the crystal and its twin which will allow simultaneous X-ray reflection

from the $\bar{1}122$ plane of one and the basal plane of the other. This is the proposition stated in the original article. Since B' is the pole of the basal plane of the twin, and C_2 is the pole of one of the desired prismatic planes of the original crystal, the proposition will be proved if it can be shown that it is possible to orient the system so that simultaneous X-ray reflection can be produced from B' and C_2 .

To do this, it is necessary to keep B' on its broken circle, and to change the position of C_2 until it lies on its appropriate broken circle (the one of smaller radius). This can be done by rotating the crystal and its twin on the axis of rotation, shown in the stereographic projection, about 25° in the direction indicated. Point B' moves to position RB' and point C_2 to RC_2 , the letter R merely signifying that a rotation has been performed.

The angles recorded in the article were calculated directly from a model of the zinc lattice. Unfortunately, in calculating the values on page 244 some errors crept in, and I want to thank Dr. McKeehan for noting these errors and correcting the values of the angles.

The objection raised by both Dr. McKeehan and Professor Mathewson about the lack of rotation of the specimen during the X-ray examination of the fractured surfaces is best answered by the consideration at the top of page 265. The cleavage surfaces were not true planes, but were curved surfaces, as was shown by reflecting a beam of light from different sections of these surfaces. The amount of curvature (approximately 4°) was sufficient to have allowed reflection from both basal and prismatic planes had they both been present in the surfaces.

Quantitative Spectrum Analysis*

By F. TWYMAN,† F. R. S., AND D. M. SMITH, B. SC., LONDON, ENG.

(Detroit Meeting, September, 1927)

PART I.—QUALITATIVE SPECTRUM ANALYSIS

THOSE chemists (they are still greatly in the minority) who use the spectroscope, use it very often, and find it almost indispensable. As a means of detecting minute quantities of the metals it is unrivalled. A metal can be readily distinguished in the presence of any other element, compound, or mixture without the necessity of separation. The qualitative analysis of the metallic constituents of a substance, which the spectroscope gives so easily, is a sure basis for planning a chemical analysis. As the determination of each element proceeds the purity of precipitates may be checked as often as desired.

If, possessing these advantages, the spectroscope has been neglected in general chemistry, it is not surprising that it was neglected in metallurgical chemistry; for many of the impurities which are of industrial interest, even when they are present in a metal or alloy in small quantities, are not then always easily detected by the examination of their visible spectrum. The history of the development of the art has been given in Bureau of Standards *Scientific Paper* No. 444.

THE DEVELOPMENT OF ANALYSIS BY SPECTROGRAPHY

Fig. 1 shows, by means of photographs taken with a quartz spectrograph, what a valuable region of the spectrum is excluded if one has a visual instrument only. Wave length 4023 is about the end of the visible spectrum, the region from 3800 to 1854 being invisible. It is easy to understand then how it is that the vigorous resuscitation of spectrum analysis which has commenced in the last few years has been associated with the use of the quartz spectrograph; notwithstanding that the most useful instrument for the general inorganic chemist to have at his elbow, after the balance, is a good visual spectrometer.^{(1) 1}

The revival of spectrum analysis is to be attributed chiefly to the work of W. N. Hartley with his co-workers, and to A. de Gramont. Hartley,

* Published in part in *Chemistry and Industry* (Apr. 1, 1927); as presented here paper is considerably revised and contains much new and additional material.

† Manager, Adam Hilger, Ltd., London.

¹ Numbers in parenthesis refer to bibliography and notes on page 303.

using the condensed spark spectra of solutions of metallic salts, first noted that it is not always the strongest lines of the metal which are the most persistent when that element is present in a substance in small and decreasing amounts. Already in 1882, he had investigated the proportions of certain metals which would be evidenced in compounds by the presence of their lines in the spectrum, and had, as a result, estimated the amount of beryllium contained in certain cerium compounds.

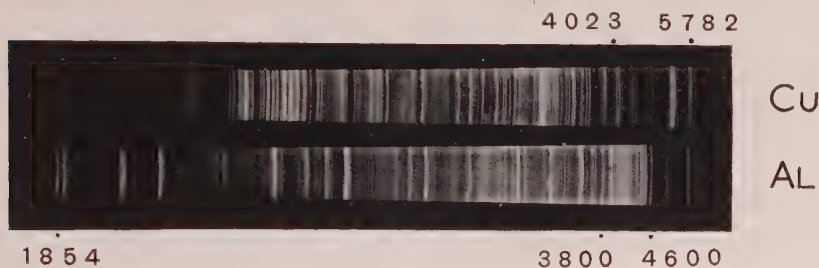


FIG. 1.—SPECTRA OBTAINED ON A QUARTZ SPECTROGRAPH.

Hartley's work was continued, also at Dublin, by Pollok and Leonard, and this group of workers, using a quartz spectrograph, studied a large number of metals. Pollok and Leonard, also using the spark spectra of solutions, distinguished certain lines of each particular metal by Greek letters, which show the degree of persistence of the spectrum line as the quantity of metal present was reduced (Tables 1 and 2).

TABLE 1.—*Pollok's Nomenclature for the Sensitive Spectrum Lines of Metals in Solution as Photographed on a Hilger Quartz Spectrograph*

To distinguish briefly between the different phases of the lines, with diminishing concentration, use has been made of some of the letters of the Greek alphabet, with the following meanings:

- τ —seen with the metal, but not with strong solutions.
- σ —seen with strong solutions, but not with 1 per cent. solutions.
- ϕ —seen with 1 per cent. solutions, but not with 0.1 per cent. solutions.
- χ —seen with 0.1 per cent. solutions, but not with 0.01 per cent. solutions.
- ψ —seen with 0.01 per cent. solutions, but not with 0.001 per cent. solutions.
- ω —seen with 0.001 per cent. solutions.

In this way Hartley and his co-workers laid the basis of an approximate quantitative spectrum analysis which he frequently used in mineralogical and other analyses. Although it is only in rare cases that this method can compare with the balance, it provides a means of readily distinguishing between a considerable percentage of a material and mere traces only, which is often very valuable. More important still, their tables render it unnecessary in hunting for a small quantity of a substance in a sample to look for any but the few spectrum lines known to be persistent.⁽²⁾

TABLE 2.—*Quantitative Spectrum of Cobalt Chloride*

Wave length	Intensity and Persistency	Wave length	Intensity and Persistency
4531.1	4 σ	3412.8	7 ϕ
10		3405.3	8 ψ
4469.7	1 σ	15—17	
4121.5	8 ϕ	3086.9	6 ϕ
4118.9	8 σ	3072.5	6 ϕ
12		18—21	
3995.5	8 ϕ	2694.7	8 ω
13		22	
3894.2	10 ψ	2663.6	8 χ
3873.2	10 ψ	23—24	
3845.6	10 ϕ	2587.2	8 ϕ
14		2582.3	8 χ
3502.4	8 χ	2580.4	8 ψ
3489.5	10 ϕ	2564.2	8 ϕ
3474.1	10 χ	2559.5	8 χ
3465.9	8 ϕ	25	
3453.6	8 ψ	2528.7	7 χ
3449.6	7 ϕ	2525.1	7 χ
3443.8	7 ϕ	2519.0	8 ω
3443.2	7 ϕ		

A. de Gramont, working on the spark spectra of solids, found that the persistent lines (which he called "Raies sensibles"): (1) were not always the strongest lines in the spectrum of the pure metal; (2) are present in the spark, but belong to the arc spectrum of the element where they are generally of great intensity, and (3) are generally present also in the spectra of very hot flames (oxyhydrogen or oxyacetylene).

A number of A. de Gramont's lines are shown in Table 3.

A. de Gramont found that these conclusions hold for alloys, minerals and fused salts, and states that his observations are in general agreement with those of Pollok and Leonard in the case of solutions, which greatly increases the value of the tables of all these observers. It is wise, however, to refer to the tables of both groups of workers; for Hartley, Pollok and Leonard give lines which A. de Gramont omits and vice versa. The order of sensibility is that found by photography, either with a quartz or with a uviol crown glass spectrograph and it is in the ultra-violet that the "raies ultimes" almost always lie. But where "raies sensibles" are recorded in the visible spectrum they are often of high sensibility for the eye.⁽³⁾

A. de Gramont applied the spectrograph to the analysis of minerals such as galena, argyrite and silico-aluminates. Utilizing the persistence of the "raies sensibles" he obtained tables for the quantitative estimation

TABLE 3.—*Rays of High Sensitivity and Ultimate Rays of the Elements (A. de Gramont)*
 [All Wave Lengths in Table Are in International Angstroms.]

SYMBOL	BY VISUAL OBSERVATION	BY PHOTOGRAPHY	
		CROWN UVIOLET SPECTROGRAPH	QUARTZ SPECTROGRAPH
Mo Molybdenum.....	5570.5; 5533.2; 5506.5	3903.0 ^a ; 3864.1 ^a ; 3798.3 ^a ; 3655.2	
Nd Neodymium ³		4303.6; 4177.3; 3951.2	
Ne Neon ¹			
Ni Nickel.....	5476.9; 5081.1; 4714.4	3619.4; 3524.5; 3515.1; 3414.8 ^a ; 3380.6; 2437.9; 2416.2 ^a ; 2316.1 ^a ; 2303.0 ^a	2802.2; 2676.0 ^a ; 2428.0 ^a
Au Gold.....	6278.2; 5837.4; 4792.6		
Os Osmium ¹			
O Oxygen ²			
Pd Palladium ⁴	5547.0; 5295.6; 5163.8	3634.7 ^a ; 3609.6 ^a ; 3421.2; 3404.6 ^a	2555.0; 2553.3 ^a ; 2535.6 ^a ; 2534.0
P Phosphorus.....		3966.4 ^a ; 3923.0; 3268.4	3064.7; 2929.8; 2659.4
Pt Platinum ³	5475.8; 5390.8; 5301.0; 5227.6	4057.8 ^a ; 3683.5 ^a ; 3639.6	2614.2; 2203.6; 2175.8
Pb Lead.....	5608.9; 5005.5	4047.2 ^a ; 4044.2 ^a ; 3447.4; 3146.4	
K Potassium.....	7699.0; 7669.4; 5832.0; 5801.8; 5782.4		
Pr Praseodymium ¹		(4825.9; 4682.2; 3814.5) ^a	
Ra Radium ¹		3799.3; 3692.4; 3658.0; 3434.9 ^a	
Rh Rhodium ⁴		4215.6 ^a ; 4201.8 ^a	
Rb Rubidium.....	7947.6; 7800.3	3499.0 ^a ; 3436.7	
Ru Ruthenium ⁴			
Sa Samarium ¹			
Sc Scandium ⁴			
Se Selenium ²	6370.9; 6346.8	4246.9; 3651.9; 3630.8 ^a ; 3613.8 ^a	
Si Silicon.....		3905.5	2881.6 ^a ; 2528.5; 2516.1 ^a ; 2506.9

² Gives neither ultimate rays nor highly sensitive rays.

⁴ Studied only with crown violet; provisional results.

^a Runge and Precht.

¹ Not studied by the author.

³ Being studied; provisional results.

^a Masked by rays of iron.

of silver from 0.0001 to 1 per cent. in lead, alloys, and minerals, and traces of other metals such as titanium and niobium in fused salts.

MODERN SPECTROGRAPHS, AND WAYS OF USING THEM

The instruments with which Hartley and A. de Gramont first worked, although quartz spectrographs, were not of the modern convenient kind. As the work done by A. de Gramont, Hartley, Pollok and Leonard was published, it became obvious that for general use a convenient photographic instrument was needed, and in 1909 one of us designed the fixed adjustment quartz spectrograph which, with slight modifications, is that in general use at the present time (Fig. 2). In 1912, in order to deal more readily with the very complex spectra of modern steels, a still larger size quartz spectrograph was made, giving three times the dispersion of the former one. Details of these instruments are readily available.⁽⁴⁾

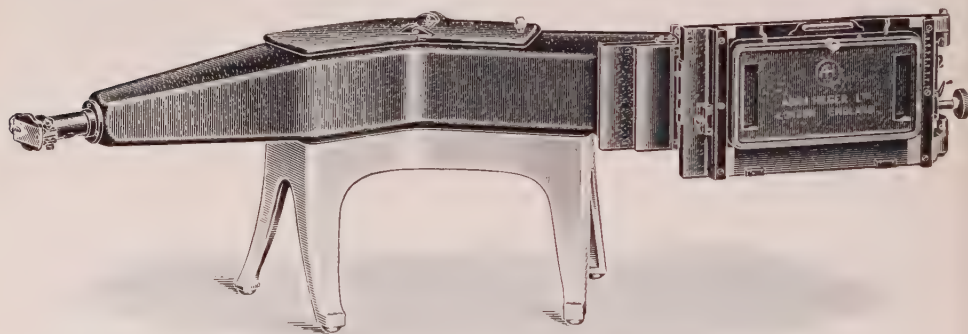


FIG. 2.—QUARTZ SPECTROGRAPH USED IN QUANTITATIVE ANALYSIS.

Now let us briefly describe the process of taking a spectrogram. The information is amply available elsewhere but the technique recommended is that which experience has shown will cover practically every variety of case likely to arise, while to obtain the same information from other sources, the searcher would have to spend many laborious hours.

LIGHT SOURCE

There are four main ways of producing from a substance radiation suitable for its spectroscopic analysis; by the flame, the arc discharge, the spark discharge, and the vacuum tube discharge.

In the flame it is only certain metals which emit radiations capable of analytical interpretation. In the arc all the metals and in addition the five non-metals, carbon, silicon, boron, phosphorus and arsenic, reveal their presence by characteristic spectra. In the spark many of the non-metals, among them fluorine, chlorine, bromine, iodine, oxygen, nitrogen,

sulfur and selenium, become detectable as well as the metals, and the method is applicable to solutions as well as solids, which is not the case with the arc.² With the spark, "air lines"³ are usually in evidence, but these can be removed by the use of a self-induction coil, as described later.

Under ordinary conditions in the vacuum tube the substance of the electrodes gives no spectrum, the lines present being only those of the rarefied gas in which the discharge takes place.

The wave lengths of the spectrum of a metal are not affected either by its state of chemical combination, or by the presence of other metals.

Flame Spectra.—Every chemist is familiar with the production of flame spectra. They are obtainable from certain metals or their salts when these are put into a Bunsen flame. Innumerable variants of this device are to be found in the mass of literature which has accumulated since the time of Bunsen, who originated this method in 1859, but it suffices to state here that as far as analytical purposes are concerned:

(a) Flame spectra are of value only in identifying the alkali and alkaline earth metals with the addition of indium and thallium.

(b) A spectroscope of low dispersion and high luminosity is the best.

(c) The ultra-violet spectrum in flame spectra being too weak to have any value for analysis, a visual spectroscope is all that is required.

(d) Although in the case of sodium the phenomenon lasts a considerable time, yet in other cases such as those of potassium and rubidium it is very evanescent, and the observation should therefore be made at the instant of introducing the salt into the flame.

Arc Spectra.—Arc spectra are, we think, the most generally useful, and when electric supply at from 150 to 220 volts D. C. is available the production of the arc between metal electrodes is very simple. When the voltage available is less than this, or when A. C. only is available most metallic arcs will not run; but the difficulty may be avoided by using carbon electrodes, and putting the substance to be examined on the lower pole.

A simple hand feed arc lamp is connected to the supply through a resistance, a current of from 3 to 6 amp. being used. Electrodes, as pure as possible, of carbon, copper or iron, or of the metal to be examined, are used and the arc is struck by allowing the electrodes to touch and then separating them by 2 or 3 mm. The following procedures suffice for practically all cases likely to arise.

Metallic Specimens.—Where the specimen is in the form of metallic rods or metallic pieces large enough, these can themselves be used as electrodes.

² The last-named eight elements do not, however, give their spectra under such conditions as to render their spectroscopic detection in a substance generally feasible.

³ *I.e.*, lines of oxygen and nitrogen.

Small Metallic or Other Specimens, Powders, Precipitates, Dry Residues from Solutions, Etc.—Carbon electrodes as pure as possible are used, and a small cup is scooped out in the lower carbon. Into this the specimen is dropped and the arc struck. A variant of this procedure is to use copper electrodes, a few milligrams of the substance being placed on the lower copper pole when the latter is hot. The substance adheres to the pole, and the spectrum of its metallic components is observable for some time.

Spark Spectra.—The apparatus required for producing the spark consists of an induction coil, or preferably, a $\frac{1}{4}$ -kw. transformer giving 15,000 volts on open circuit, with a condenser and self-induction coil. If alternating current is not available, a small converter must be added. These are arranged as in Fig. 3.

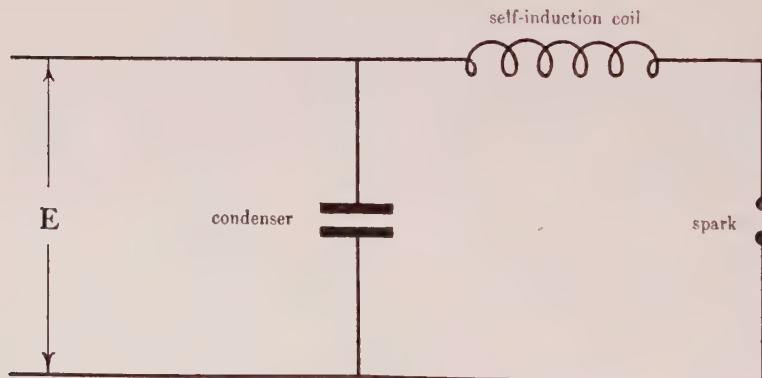


FIG. 3.—ARRANGEMENT OF SPARK APPARATUS.

Solids, Including Powders.—The specimens for sparking are held in clips in an adjustable holder. This holder suffices for metals, alloys or conducting minerals. If the specimens consist of nonconducting powders (such as those of slags, precious stones, stony minerals, glasses, precipitates or residues from solutions), there should be added a small cup of platinum of about 15 mm. dia. and 3 mm. deep, held in the lower clamp by a wire of the same metal, the cup being heated in the flame of a Meker burner. A stout platinum wire leads the spark from the upper clamp to the platinum cup, in which the powder or powdered mineral is mixed and fused with about four times its weight of sodium or lithium carbonate—these salts being chosen because of the simplicity of their spectra.

Liquids.—If the samples are in the form of solutions, the sparking tubes of Hartley or of Pollok may be adopted.⁽⁵⁾

Another class of cases, which may be considered here, is that in which a substance of relatively high volatility is to be looked for; for instance, zinc in small quantity in, say, an organic substance. It may be preferred on general grounds to use the arc, and in that case the hollowing out of a space in the bottom electrode (preferably cored) of a carbon arc is the method indicated, but for a volatile substance this hole should be deep and this desideratum becomes the more necessary if the substance is of an organic nature or damp, in which case it is very likely, if the hole in which it is placed is not deep, to jump out of position before the examination can be even commenced.

In cases of this kind a visual examination is often very successful; the observer having started the arc has plenty of time to sit at the spectroscope and watch until the arc burns down to the substance to be examined. Very minute quantities can thus be observed, however evanescent the appearance of the lines. Of course, difficulties are likely to arise from the presence of impurities in the arc, and to avoid this, very pure carbons have been put on the market, but we are speaking at the moment of more volatile metals, which are easily driven off by a few minutes' running of the arc, or at least brought to a state of constant and low intensity.

So much for how the sample is made to emit the light. Next will be described very briefly the means of identifying the lines of the various elements.

COMPARISON SPECTRA

In Fig. 4 the spectra of several samples are shown close together. These spectra are taken one after the other on the same plate without any readjustment of the spectrograph. If there are any constituents common to two or more of the samples the spectrum lines of those constituents will appear in the corresponding spectra. Spectra so arranged are called "comparison spectra."

To Ascertain Whether a Substance Contains a Specified Metal.—Three spectra are taken, of which the first is that of any metal which is known to be present in considerable quantity, or if none such be known then one of the purest iron obtainable; the second that of the sample under test; while the third is that of the metal whose presence or absence is to be determined.

The set of photographs develops like that shown in Fig. 4, in which the bottom spectrum is zinc of very high purity, the middle spectrum that of the commercial spelter under examination and the top spectrum that of cadmium, the metal whose presence or absence is in question. It will be seen by the presence of the sensitive cadmium lines of wave lengths 3261.1 and 3610.5 that the spelter contains cadmium, while the

sensitive copper lines 3247.5 and 3274.0 show that this is present in the cadmium, the spelter, and even in the zinc. It is not, of course, necessary to adopt this precise arrangement of spectra, but it is one that is very frequently convenient.

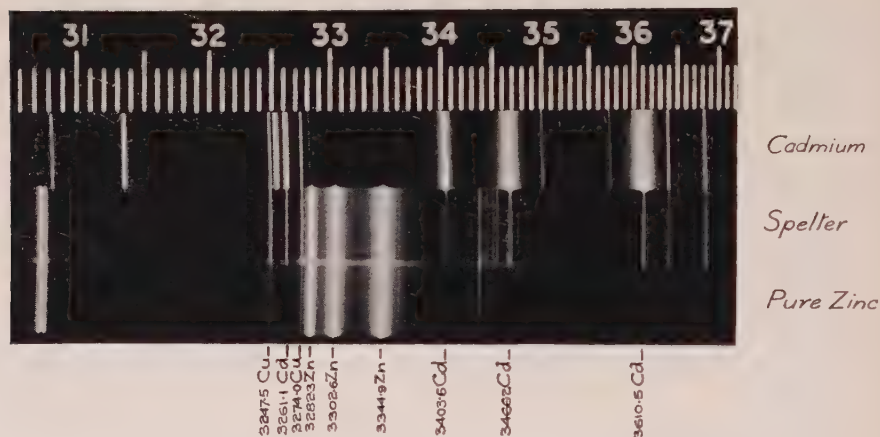


FIG. 4.—"COMPARISON SPECTRA."

If examinations for the presence of other metals are required to be made on the same sample or if other samples are to be tested, the same plate can be used by racking the dark slide to a fresh position, and as many as six strips (that is, 18 spectra in all) will easily go on a single plate. By such methods all the metallic constituents in an alloy, mineral, ash, or what not, can be readily and quickly identified.

PART II.—QUANTITATIVE SPECTRUM ANALYSIS

Variation of Intensity with Content

We have seen how Hartley, with his co-workers, endeavored to found a quantitative method of spectrum analysis on the observation of the amount of dilution to which a solution could be submitted before the disappearance of certain distinctive lines which he called "persistent" lines. The method has the disadvantage that a solution must be made up and the avoidance of the making-up of solutions is among the advantages of spectrum analysis.

Of recent years, therefore, attempts have been made in the laboratory of Adam Hilger, Ltd., and elsewhere, to found a method of quantitative analysis on observations of the varying intensities of the spectrum lines with the proportion of the corresponding ingredients. It is true attempts

of the kind were made many years ago, and were not very successful. Recent attempts, however, have been more so.

If we take any range of percentages of particular impurities in a particular metal we shall find that there are certain lines which do not alter much in intensity, while there are usually other lines which alter rapidly in intensity. Obviously, in attempting a quantitative determination of a substance which is present in approximately, say, 10 per cent., we should utilize for our observations not the lines which do not alter in intensity round about that percentage, but those which do. These are not generally the persistent lines or "raies sensibles" and, since there has been no large accumulation of data relative to these variable lines of a character similar to that accumulated by Hartley, A. de Gramont, and others for the persistent lines, each observer will usually, for the time being, find it necessary to accumulate the data for himself. A certain amount of such information has been collected in our laboratory, using Hilger instruments, and we will now give a brief account of some of the examples of quantitative analysis the routine of which has been worked out.

The instrument used by us is the quartz spectrograph, usually the size shown in Fig. 2, which gives a spectrum 230 mm. long from 2000 to 10,000 Å. Either the arc or spark spectrum is used for this work, and in most cases the arc method is both simpler to use and more sensitive in detection.

A convenient form of arc is obtained by using two electrodes of the metal under examination, and maintaining an arc about 5 mm. in length by a current of about 3 amp. This can be obtained, using a D. C. supply of 220 volts and placing in series with the arc a lamp resistance having four 50-c.p. carbon filament lamps in parallel. It is preferable to have both electrodes of the material under test, as in that case no additional impurities are introduced. If only one piece of the metal is available, such as copper, it is advisable to use the sample as positive electrode and a rod of the purest copper obtainable as negative electrode. In the same way for analyzing steel samples the negative electrode would be pure iron. This method has the disadvantage that the intensities of the impurity lines are less than would be the case if both electrodes were of the same material.

In the case of the spark, using an A. C. supply of 150 volts and transformer as described above, a satisfactory spark will be obtained (about 5 mm. in length) by placing four lamps in the lamp board; and this is the procedure which has been regularly adopted. An image of the spark or arc is thrown on the slit of the spectrograph by means of a quartz condensing lens.

The most suitable shape of spark electrodes is wedge-shaped, so that they can be mounted in the holders with the edges of the wedge parallel to, and in line with the axis of the collimator. This arrangement gives a

steady image on the slit. Whatever the shape of the electrodes, however, it is advisable to mount them in the holders so that the discharge takes place either in this manner, or from two points, so as to obtain an image on the slit which does not wander.

It has been criticised that the spectrum obtained by using rods or lumps of the metal under examination as electrodes is representative only of the spots of the electrodes between which the discharge is taking place, and perhaps not of the main bulk of the metal. On the other hand, a method such as this, which will detect segregation of impurities, has very much to commend it. Also, when wedge-shaped electrodes as described above are used it will be observed that the discharge wanders along the edge of the wedge and hence a more representative result will be given; and in any case, if a number of specimens be taken from the same sample and an average result deduced from a consideration of their spectra, a fairly representative result will be obtained.

An alternative method is to obtain a representative sample from the bulk of the metal and dissolve it in acid and obtain a solution of known concentration with respect to the weight of the sample. This solution is then used as the sample for spectroscopic investigation. This amounts practically to the method of Hartley, Pollok and Leonard, with its attendant dangers of introduced impurities.

Where the sensitive lines used in analysis lie towards the ultra-violet end of the spectrum the ordinary condensed spark generally proves satisfactory, but when the lines occur towards the visible part of the spectrum trouble arises from the "air lines" (lines due to oxygen and nitrogen) which may mask the lines of the material, especially if these are faint. To remove these air lines from the spectrum a self-induction coil is placed in series with the spark, as shown in Fig. 3.⁽⁵⁾

The method of quantitative spectrographic analysis now to be described is based on the appearance and variation of intensity of selected lines in the spectra of standard samples. As the percentage of impurity increases, other lines than the sensitive lines of A. de Gramont begin to appear, these lines showing an increase in intensity as the amount of impurity increases. These lines are readily identified by photographing a comparison spectrum of the impurity itself. It has been found, as explained above, that the actual "raie ultime," or "raie sensible," which appears when only traces of the impurity are present, is not always the best line to use in quantitative work. Any lines which appear with certain percentages of the impurity, and show a systematic variation of intensity can be used, and those are best which vary most rapidly with variation of percentage.

In the preparation of standard alloys containing definite percentages of each metal, the Ajax-Northrup induction furnace is recommended by the Bureau of Standards.⁽⁷⁾ Homogeneity of the alloys and minimum loss from volatilization and freedom from contamination are then insured

The purity of the metals used in the preparation of these synthetic alloys can, of course, be checked by spectrographic methods.

Having standard samples whose impurity contents are accurately known, their arc spectra are photographed in juxtaposition on the spectrograph. The wave-length scale (which is photographed directly on the plate) facilitates the identification of the sensitive lines in the spectra; but to make the identification still easier, a further spectrum can be photographed, namely, that of a sample of the metal for which estimations are to be carried out. In the various spectra these sensitive lines

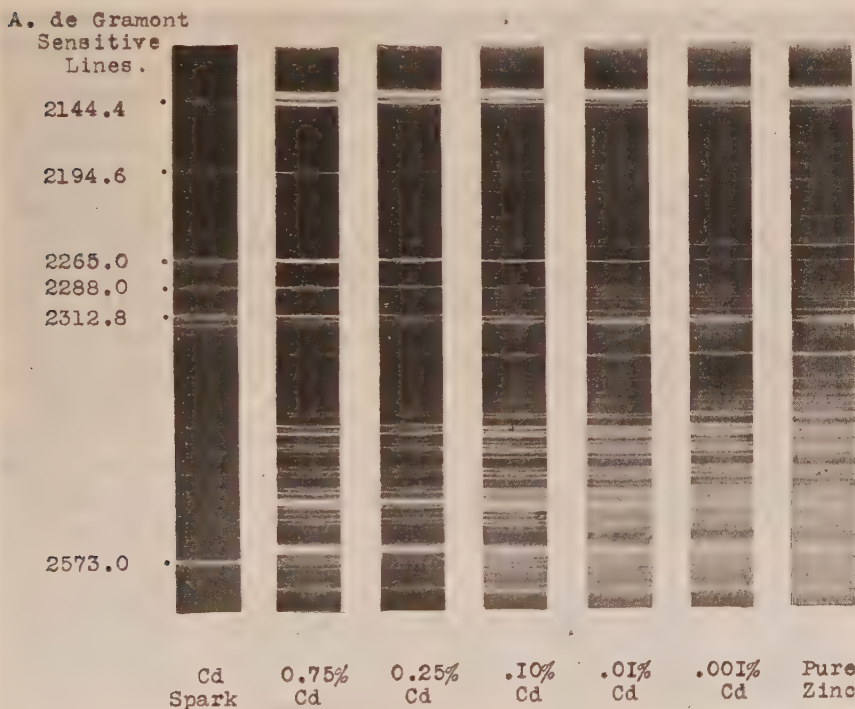


FIG. 5.—SPECTROGRAPHIC ESTIMATION OF CADMIUM IN ZINC. $\times 3$.
The pure zinc was a sample redistilled under very exceptional precautions.

will decrease in intensity as the percentage of impurity is decreased, and in some cases will disappear. Hence, using these spectra as standards, spectra of any samples of a like composition can be compared with them and estimations made within the range of the standard samples. It sometimes happens that a sensitive line due to the impurity occurs fairly close to a line of the metal containing that impurity. In this case the estimation is considerably simplified, as the line due to the main bulk of the metal serves as an intensity standard, and any errors which may arise from differences in exposures and developing are eliminated.

This procedure has been clearly described by W. Gerlach:

"Two lines of the impurity are not compared with one another, but one (or more) lines of the impurity B with one (or more) neighboring lines of the substance containing it, as far as possible equal in intensity. A single ideal case will serve to illustrate this. Near a spectrum line λB of the impurity B occur three lines of the main substance A , $\lambda_1 A$, $\lambda_2 A$, and $\lambda_3 A$. Adopting these three lines as standards one finds that the intensity of the λB line

At 1.0 per cent. is equal to $\lambda_1 A$

At 0.2 per cent. is equal to $\lambda_2 A$

At 0.05 per cent. is equal to $\lambda_3 A$

Then in the analysis of the substance $A + x$ per cent. B the quantity x is determined from the brightness of the B line relative to $A_1 A_2 A_3$. This method is already well developed, and gives results whose accuracy increases as the range between the standards decreases. Also it is independent of photographic effects."⁽⁶⁾ (*Translation.*)

As a result of spectrographic investigations which have been carried out in the Hilger laboratories with various metals, it may be stated that one can distinguish between 0.001 per cent., 0.01 per cent., 0.1 per cent. and 1.0 per cent. of any metallic impurity by such comparisons of the intensities of the lines; while in favorable cases (Fig. 5) a very much higher accuracy is attained. The estimation is, of course, very rapid— $\frac{1}{2}$ hr. will suffice for the whole procedure of photography, developing and estimation; and the plate forms a permanent record of the whole metallic contents of a sample.

The tables of Hartley, Pollok and A. de Gramont are useful whether the arc or spark be used, since the lines which are persistent in the spectrum of the spark are persistent also in that of the arc. At the same time it should be observed that where one is dealing with a small quantity of metal of high melting point (such as iron or nickel) in a metal of low melting point (such as copper or aluminum) the arc is not so sensitive as a means of detection of impurity, the reason probably being that there is an insufficient quantity of the vapor volatilized in the arc, the temperature of which is low as a result of the low boiling point of the main bulk of the metal.

SPECIFIC EXAMPLES OF QUANTITATIVE ESTIMATIONS

*Determination of Small Quantities of Cadmium, Lead and Iron in Zinc*⁴

This research was carried out for the British Non-ferrous Metals Research Association, who supplied very carefully prepared samples of zinc and graduated alloys for standards, including one sample from the New Jersey Zinc Co., prepared by fractional distillation after electrolytic refining, and considered to be spectroscopically pure.

⁴ Reproduced by permission of the British Non-ferrous Metals Research Association.

It was found that with Schumann⁵ plates an exposure of 2 min. of the condensed spark between two pieces of the zinc sample was sufficient, and satisfactory results could be obtained with Wellington anti-screen plates coated with a thin film of paraffin oil, giving an exposure of 5 min. Ordinary paraffin oil is wiped on the film side of the plate with a piece of chamois leather, obtaining as thin a film as possible. Then the plate is exposed for the required time, and before development the oil is removed with a piece of cotton wool soaked in benzene. Methylated spirits will also remove the paraffin oil, but benzene possesses the advantage that it evaporates very quickly and any traces of oil remaining can be seen and wiped off.

1. *Estimation of Cadmium in Zinc.*—The following table was obtained from a series of spark spectra of zinc samples containing various amounts of cadmium:

Cadmium 0.75 Per Cent.	Cadmium 0.25 Per Cent.	Cadmium 0.1 Per Cent.	Cadmium 0.01 Per Cent.	Cadmium 0.001 Per Cent.
2573.0	2573.0 (Just visible)			
2312.8	2312.8	2312.8		
2288.0	2288.0	2288.0	2288.0	
2265.0	2265.0	2265.0	2265.0	2265.0
	(Masked by zinc line)			
2194.6	2194.6	2194.6	2194.6	
2144.4	2144.4	2144.4	2144.4	2144.4

The two lines $\lambda 2144.4A$ and $\lambda 2573.0A$ are of special importance since from the appearance of these lines alone the estimation can be carried out.

The line $\lambda 2573.0A$ appears faintly between two zinc lines when there is 0.25 per cent. Cd present, and is of approximately the same intensity as the two zinc lines when 0.75 per cent. Cd is present.

The relative intensities of the cadmium line $\lambda 2144.4A$ and the neighboring zinc line at $\lambda 2147.4A$ enable one to distinguish between the presence of 0.001 per cent. Cd, 0.01 per cent. Cd and 0.1 per cent. Cd as follows:

0.001 per cent. Cd. Cadmium line fainter than the zinc line.

0.01 per cent. Cd. Both lines of approximately the same intensity, the cadmium line just a little stronger than the zinc line.

0.1 per cent. Cd. Cadmium line much more intense than the zinc line.

The arc method of analysis also yields results suitable for routine quantitative analysis. The following table was prepared from the arc spectra of the same samples:

⁵ Photographic plates having the minimum amount of gelatin necessary to hold the emulsion. They are consequently very sensitive to the ultra-violet part of the spectrum.

Cadmium 0.75 Per Cent.	Cadmium 0.25 Per Cent.	Cadmium 0.1 Per Cent.	Cadmium 0.01 Per Cent.	Cadmium 0.001 Per Cent.
3610.5	3610.5	3610.5		
3466.2	3466.2	3466.2	3466.2 (Barely visible)	
3403.6	3403.6	3403.6		
3261.1	3261.1	3261.1	3261.1	
2980.6	2980.6	2980.6		
	(Faint)	(Faint)		
2880.0	2880.8 (Barely visible)			
2288.0	2288.0	2288.0	2288.0	2288.0
2265.0	2265.0	2265.0	2265.0 (Faint)	
2144.4	2144.4	2144.4 (Faint)		

2. *Estimation of Lead in Zinc.*—Both the arc and spark methods of analysis were investigated for the quantitative determination of lead in zinc and the arc method was found to be far superior to the spark method. The three zinc arc lines $\lambda\lambda 4810.5A$, $4722.2A$ and $4680.2A$, are available as intensity standards, following the method proposed by W. Gerlach.⁽⁶⁾

TABLE OF SENSITIVE LEAD LINES APPEARING IN THE ARC SPECTRA OF ZINC-LEAD ALLOYS

0.092 Per Cent.	Lead 0.1 Per Cent.	Lead 0.01 Per Cent.	Lead 0.009 Per Cent.
4057.8	4057.8	4057.8	4057.8
3740.1	3740.1 (Barely visible)		
3683.5	3683.5	3683.5	3683.5
3639.6	3639.6	3639.6	3639.6 (Faint)
3572.7	3572.7 (Barely visible)		

It will be noted that the intensity of the lead lines in the sample containing 0.092 per cent. lead by analysis indicates a higher percentage than in the standard sample containing 0.1 per cent. of lead. Hence, until further work is done it would appear unsafe to use spectrographic methods for lead except in quantities below 0.1 per cent. The estimation of lead in the sample containing 0.009 per cent. lead by analysis indicates an amount slightly less than the 0.01 per cent. lead in the standard sample, and for such quantities the spectrographic method would apparently give reliable results.

In the case of the spark spectra, the lead line $\lambda 2203.7A$ appears in the spectra of 0.092 per cent. lead and 0.1 per cent. lead, but is absent

in those of 0.01 and 0.009 per cent. lead. The lead spark line is therefore not so sensitive as the lead arc lines and hence for quantitative determinations, the arc method is preferable in the case of zinc-lead alloys.

3. *Estimation of Iron in Zinc.*—Owing to the very large number of sensitive lines in the iron spectrum, the identification and comparison of suitable lines is not so simple a matter as in the case of cadmium or of lead. Also in this case a spectrograph with a comparatively large dispersion is more suitable for the work (such as the Hilger E.3); whereas for lead and cadmium the smaller E.37 suffices.

TABLE 4.—*Sensitive Iron Lines Appearing in the Spark Spectra of Zinc-iron Alloys*

(p = present; f = faint; bv = barely visible)

W. L.	Percentage Iron						
	Iron, 0.108 Per Cent.	Iron, 0.1 Per Cent.	Iron, 0.053 Per Cent.	Iron, 0.05 Per Cent.	Iron, 0.01 Per Cent.	Iron, 0.008 Per Cent.	Iron, 0.0032 Per Cent.
2755.74	p	p	p	p	bv		
27 3.29	p	p	p	bv			
2749.32	p	p	p	p	f	bv	
2746.99	p	p	p	p	bv		
2746.49	p	p	p	p	bv		
2743.20	p	p	p	p			
2739.55	p	p	p	p	f		
2730.74	p	p	p	f			
2720.91	p	p	f	bv			
2719.04	p	p	f	bv			
2704.00	p	f					
2692.66	p		bv				
2666.64	p	p	bv				
2664.67	p	p					
2631.33	p	p	p	p	bv		
2631.05	p	p	p	p	bv		
2628.30	p	p	p	f			
2625.68	p	p	p	p	bv		
2621.68	p	p	p	p			
2617.63	p	p	p	p			
2613.84	p	p	p	p			
2611.89	p	p	p	p	bv		
2607.10	p	p	p	p			
2599.41	p	p	p	p	p		
2598.38	p	p	p	p			
2592.80	p	f	bv				
2591.55	p	f	bv				
2585.89	p	p	p	p	bv		
2413.31	p	p	p	p			
2411.07	p	p	p	p			
2410.53	p	p	p	p			
2406.66	p	p	p	p			
2404.89	p	p	p	p			
2399.24	p	p	p	p	f		
2395.63	p	f	p	p	p	bv	
2388.63	p	p	p	p	bv		
2382.04	p	p	p	p	p	bv	bv
2380.76	p	f	bv				
2379.28	p	f	bv				
2375.19	p	p	p	f			
2373.73	p	p	p	p			
2368.60	p	p	p	bv			
2364.82	p	p	p	p			
2360.31	p	p	p	p	f		
2359.97	p	p	p	f			
2359.12	p	p	p	f			
2345.32	p	f	bv				
2344.31	p	p	p	bv			
2343.50	p	p	p	p			
2337.99	p	p	p	p			
2332.74	p	p	p	p			
2331.29	p	f	bv				
2327.37	p	f	bv				

To give the best results, where both iron and cadmium are to be estimated together, either Schumann plates or paraffin-coated Wellington anti-screen plates, should be used; for iron alone Wellington anti-screen plates, uncoated, are quite suitable.

It was found that the tables of Hartley for iron chloride (⁽⁵⁾ p. 42), and of A. de Gramont (p. 82, *ibid.*), though ample for establishing the presence of iron in small quantity, did not record enough lines of graded sensitiveness for quantitative analysis. On the other hand, the more complete and accurate wave lengths in the iron spectrum published in Kayser and elsewhere, give no guidance at all concerning which lines appear when small quantities are present. Hence, the Table 4 was prepared from spectrograms taken for this purpose on Hilger quartz spectrographs, size E.1 and E.3:

When 0.05 per cent. Fe is present in the zinc, the iron line $\lambda 2388.63A$ and the neighboring zinc line $\lambda 2390.20A$ are of approximately the same intensity.

Hence it has been shown that to a great extent the difficult and tedious chemical assay of cadmium, lead and iron in zinc can be replaced by the spectrographic method, bearing in mind the limitations referred to above.

Impurities in Copper

Bismuth is one of the most injurious elements that can be present in copper. It induces extreme brittleness so that not more than 0.005 per cent. of bismuth can be tolerated. According to W. Stahl⁽⁸⁾ as little as 0.02 per cent. Bi renders copper hot-short, while 0.1 per cent. renders it cold-short, although the effect can be reduced to some extent by the addition of the requisite amount of antimony or arsenic. Bismuth occurs in the form of films between the copper crystals, and this is the reason of the brittleness.

Other impurities present in copper, such as arsenic and iron, seriously affect the electrical conductivity. Although the copper obtained by electrolytic refining is of exceedingly high purity, impurities are unavoidably introduced during subsequent remelting and casting. "When the amount of arsenic is small, it cannot be identified as a separate constituent under the microscope, but exists in what is called a solid solution. The consequence is in this particular case of arsenic in copper, that the mechanical properties of copper are not adversely affected until the amount of arsenic becomes considerable. On the other hand, the effect on the electrical conductivity is very great, because the presence of the arsenic atoms in the crystals themselves destroys the complete regularity of their structure and interferes with the passage of the electrons which carry the electric current."⁽⁹⁾

The main difficulty in the chemical analysis of copper with respect to bismuth is that the method consists of a very large number of manipula-

tive processes, which necessarily reduce the chances of accuracy. The determination takes considerable time, and in view of the small quantity which is usually present, and also in view of the fact that the methods are partly gravimetric, any great degree of accuracy is difficult to attain. In most instances it is desired to know rapidly what the percentage of bismuth in copper may be, so that rapid decisions regarding material can be reached, and the chemical methods are too tedious for this purpose to be achieved.

These chemical processes can be replaced by the comparatively simple spectrographic method, which is based on the intensity of the bismuth lines, wave lengths 3067.7 and 2898.04 which appear in the arc spectra of copper samples containing bismuth.

When there is 0.1 per cent. Bi present in copper, the line $\lambda 3067.74$ is approximately equal in intensity to the copper line $\lambda 3073.84$ in the arc spectrum. The bismuth line appears between the two copper lines $\lambda\lambda 3063.44$ and 3073.84 which serve as intensity standards. The bismuth line appears when 0.005 per cent. bismuth is present and is the "raie ultime." Also when 0.1 per cent. Bi is present, the line $\lambda 2898.04$ is present, but faint, and the lines $\lambda\lambda 2938.3$ and 2989.04 are barely visible and when 0.025 per cent. Bi is present, the line $\lambda 2898.04$ is barely visible.

In the same way small quantities of arsenic can be estimated from the arc spectra of copper samples containing arsenic, and the Table 5 gives the sensitive arsenic lines employed.

TABLE 5.—*Sensitive Arsenic Lines Appearing in the Arc Spectra of Copper Samples Containing Arsenic*

λA	0.87	0.54	0.42	0.40	0.36	0.325	0.275	0.245	0.195	0.11	0.03
2860.5	p	p	p	p	p	p	p	p	f	bv	
2780.2	p	p	p	p	p	p	p	p	f	bv	
2745.0	p	p	p	p	p	p	p	f	f	f	bv
2456.5	p	f	bv	bv							
2381.2	p	f	f								
2370.8	p	p	f	bv							
2349.8	p	p	p	p	p	p	p	p	f	bv	
2288.1	p	p	p	p	p	p	p	p	p	f	bv

[p indicates that the line is definitely present, f that it is faint, and bv that it is barely visible.]

The line $\lambda 2370.84$ is very close to the copper line $\lambda 2369.94$.

The arsenic lines $\lambda\lambda 2381.2$ and 2288.14 appear very near to the positions of sensitive lines due to other impurities, *viz.*, $\lambda 2382.04$ (iron) and $\lambda 2288.04$ (cadmium).

Certain copper lines are found to be available as intensity standards in the estimation of arsenic; and in the following table, the first column gives the arsenic line, the second a neighboring copper line and the third column the percentage of arsenic

present when these lines (due to arsenic and copper, respectively) are of approximately equal intensity:

λ (As)	λ (Cu)	As, PER CENT.
2288.1	2276.3	0.5
2349.8	2356.6	0.3 to 0.35
2780.2	2768.9	0.4

Determination of Calcium in Magnesium

In the use of magnesium for light alloys it is customary to add calcium to retard the rapid oxidation of the molten surface during foundry operations. If much less than 0.1 per cent. be present, the calcium has

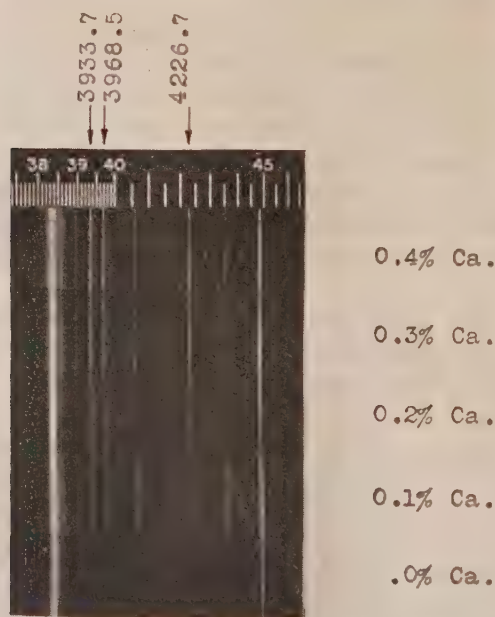


FIG. 6.—QUANTITATIVE SPECTROGRAPH DETERMINATION OF CALCIUM IN MAGNESIUM.

but little of this desired effect, while if it is present in excess of 0.2 per cent. it is not only in excess of requirements but appears to be objectionable. The accurate determination by chemical means of such small quantities of calcium is an extremely laborious process, and is also subject to uncertainty on account of the masking effect of the relatively large quantity of magnesium.

The quantitative spectrographic determination is, however, both rapid and reliable. A condensed spark discharge is passed between two pieces of magnesium under test, a self-induction coil being included in the circuit. Fig. 6 shows the increase in intensity of the calcium lines 3933.7,

3968.5 and 4226.74 as the percentage of calcium in the magnesium increases. This photograph was obtained on a Hilger E. 3 spectrograph with 3 min. exposure for each spectrum.

Determination of Aluminum in Brass

Aluminum in brass increases the hardness of the material. Furthermore, brass containing aluminum is generally found difficult to forge. Beyond these facts, however, aluminum imparts a characteristically light color to brass even when present in only small quantities, and this color renders the brass unacceptable to many people.

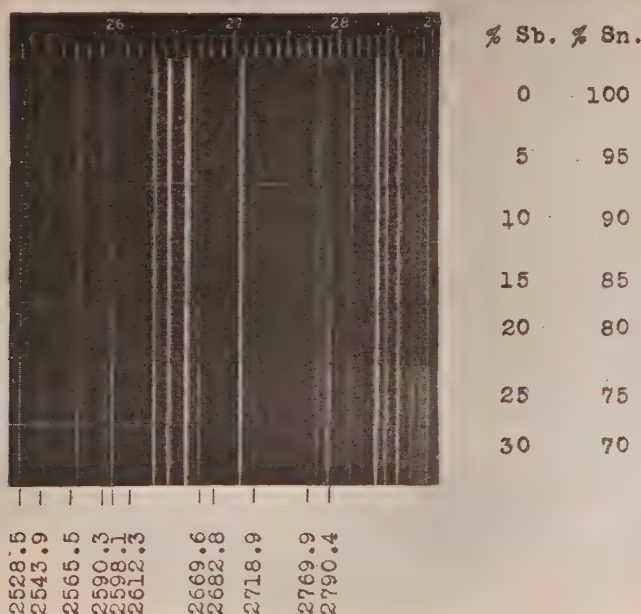


FIG. 7.—SPARK SPECTRA OF TIN-ANTIMONY ALLOY.

The aluminum spectrum is well developed in the arc spectrum of brass containing 0.64 per cent. aluminum. Hence the arc method of analysis should prove very useful for small percentages of aluminum in brass.

The difficulty in connection with the determination of aluminum in brass, by chemical methods, is that it is a long and tedious process entailing a number of operations, whereas the spectrographic method is comparatively rapid.

Spark Spectra of Tin-antimony Alloys

Two minutes' exposure of the condensed spark discharge between small pieces of tin-antimony alloy samples was given. The increase in intensity

of the sensitive antimony lines as the amount present increases to 30 per cent. in stages of 5 per cent. is shown in Fig. 7.

The line $\lambda 2598.1A$ (which is given as a "raie ultime" by A. de Gramont) appears in the spectrum of pure tin, showing that a trace of antimony is present therein.

When 15 per cent. Sb is present the antimony line $\lambda 2528.5A$ is equal in intensity to the tin line $\lambda 2546.8A$, and the antimony line $\lambda 2669.6A$ is equal in intensity to the tin line $\lambda 2665.7A$.

When 10 per cent. Sb is present the Sb line $\lambda 2790.4A$ is equal in intensity to the line $\lambda 2785.0A$.

Determination of Small Quantities of Impurities in Lead

The bismuth line $3067.7A$ and the copper doublet 3247.5 and $3274.0A$ can be used for the quantitative determination of small quantities of these metals.

Further examples of the quantitative spectrographic analysis of non-ferrous metals are given in Bureau of Standards *Scientific Paper* No. 444;⁽⁷⁾ the method adopted was to use the condensed spark with a self-induction coil included in the circuit. Spectra of various alloys are reproduced with a detailed account of the technique and mode of procedure, the metals for which quantitative results are given being tin (used for fusible safety plugs for steamboat boilers), gold and platinum. In each of these cases only minute quantities of impurities may be present and the spectrographic method is shown to be far superior to the chemical methods for their detection and estimation. The authors conclude that "quantitative spectrographic analysis applied to problems of the kinds described above is a successful procedure and one that may be readily extended to many problems in chemistry, metallurgy, mineralogy, physics, biology and other sciences."

STEEL ANALYSIS

Determination of Chromium and Manganese.—In obtaining the photographs reproduced, one minute's exposure of the arc between steel samples was given in each case, using a uviol glass spectrograph, E. 43.

It is difficult to maintain a steady arc between ferro-chromium electrodes (containing 69.5 per cent. Cr) and thus the series of spectra of chromium steels reproduced in Fig. 8 has been obtained by using the sample as the positive electrode and a pure iron rod as the negative electrode. In using pure iron as one electrode care has to be taken not to allow a bead of molten iron to adhere to the sample under investigation, otherwise the spectrum will be that of practically pure iron.

In the case of the series of spectra of manganese steels reproduced in Fig. 9, both electrodes were of the same sample, and greater variations in intensity were obtained in this way.

The lines of chromium and manganese which are found to be useful are as follows:

(a) Chromium. The group of lines 5208.4, 5206.1 and 5204.5A, shows an increase of intensity as the percentage of chromium increases, and it occurs in a region of the spectrum which is comparatively free from iron lines. These lines are given as sensitive lines by A. de Gramont.

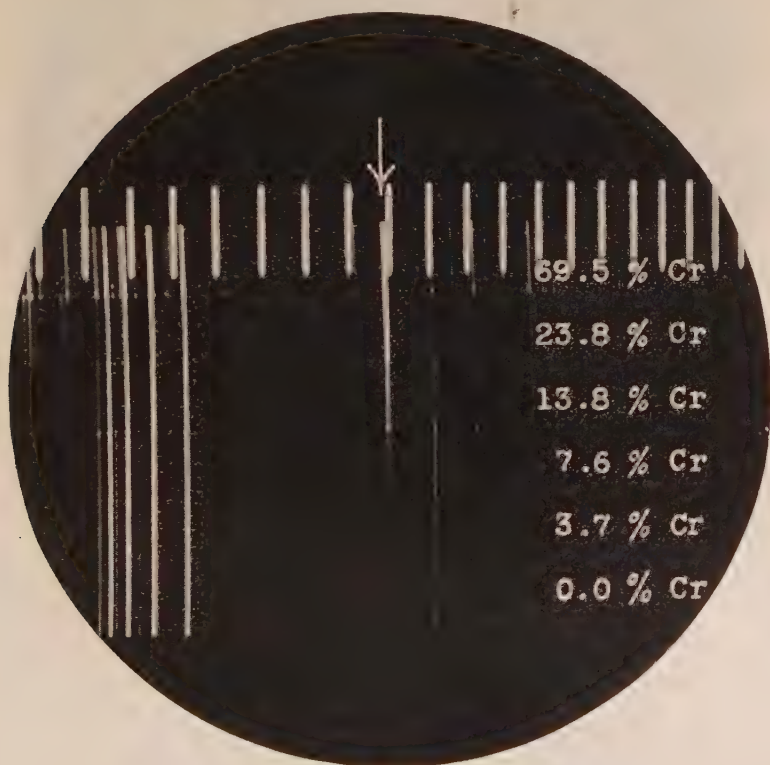


FIG. 8.—SPECTRA OF CHROMIUM STEELS OBTAINED BY USING SAMPLE AS POSITIVE ELECTRODE AND A PURE IRON ROD AS NEGATIVE ELECTRODE.

(b) Manganese. The group of lines 4761.7; 4762.5; 4766.0; 4766.6; 4754.1; 4783.5; 4823.6 gives the best variation of intensity with increasing percentage of manganese present in the steel. This group also occurs in a region of the spectrum comparatively free from iron lines. The lines 4823.6, 4783.5 and 4754.1A are given as sensitive lines in the spark spectrum by A. de Gramont, but the remaining lines are sensitive under these conditions to the same extent as the sensitive lines, although not classified as such.

Determination of Carbon in Steels.—Fig. 10 was obtained by photographing the spark spectra of carbon, and of ferromanganese and ferro-

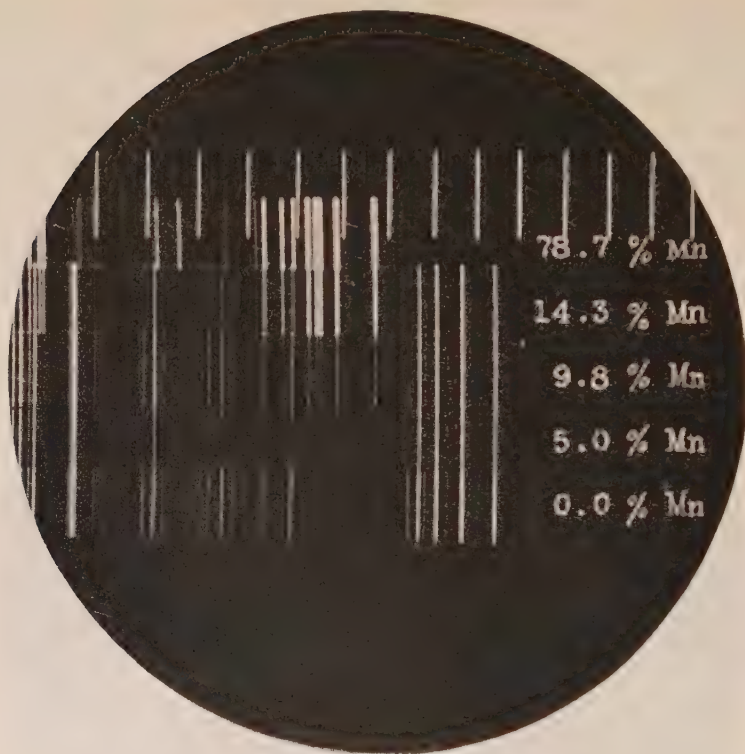


FIG. 9.—SPECTRA OF MANGANESE STEELS OBTAINED WHEN BOTH ELECTRODES WERE OF SAME SAMPLE.

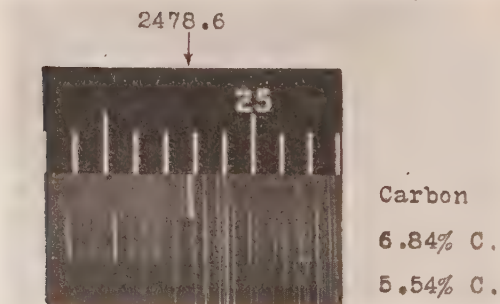


FIG. 10.—SPARK SPECTRA OF CARBON IN STEELS.

chromium containing 6.84 and 5.54 per cent. carbon, respectively. A distinct increase in intensity in the "raie ultime" 2478.64 of carbon is observed. A 5-min. exposure was given in each case, using the medium quartz spectrograph, E. 3.

Some doubt has been expressed as to the utility of such spectrographic analyses of steels. There is no difficulty whatever in estimating manganese or chromium in steel by chemical methods with a high degree of accuracy and without doubt that the determination is correct. But the comparatively rough quantitative estimations by spectrogram are obtained with great rapidity, and information as to all the other metals present is given at the same time. The method is well adapted to the sorting out of steels and checking purposes.

A visual instrument has been designed for the purpose of rapidly estimating nickel and chromium in steels. This instrument enables the presence of nickel and of chromium in samples of steel (*e. g.*, steel bars or steel scrap) to be detected immediately, even by an unskilled observer. Not only so, but a few days' experience with bars of known nickel or chromium content will enable the observer to state the approximate percentage present—as, for instance, 1, 2, or 4 per cent.

The instrument has no adjustments, the observation of nickel and chromium, respectively, being provided for by two eyepieces, in one of which are seen the most distinctive nickel lines, and in the other the most distinctive chromium lines. These lines are seen and identified by a circle around each, and by their position in relation to the iron lines grouped immediately around them, and the instructions for use of the instrument contain a description whereby the observer unfamiliar with the spectrum may find the lines without difficulty.

The arc is struck by touching both rods simultaneously with a third rod of iron or carbon steel (insulated by pushing over one end of it a piece of ordinary rubber tube). Removal of this rod strikes the arc, and the observer at the spectroscope is able immediately to state whether or not the sample contains an important quantity of nickel or chromium. With the aid of three or four standard samples containing various percentages of nickel and chromium, he can soon accustom himself to state also the range of percentage within which the nickel or chromium content lies.

We conclude this paper with a short bibliography and with extracts from both published and private communications on the general subject of the usefulness of the spectrograph in industrial laboratories.

BIBLIOGRAPHY AND NOTES

1. The visual spectroscope is often of great use in sorting tests which must be made repeatedly with as little loss of time as possible. As an instance may be mentioned a form of instrument made recently for testing steel bars in a rolling mill ware-

house to detect and approximately estimate the percentage of nickel and chromium in the steel. Three of these are in constant use in one Sheffield steel works (Messrs. Vickers, Ltd., see note on following page).

2. The results and tables of Hartley, Pollok and Leonard were published in Roy. Soc. *Phil. Trans.* (1884) Pts. I, 2; and in Roy. Dublin Soc. *Proc.* **11**, (N. S.) Nos. 16, 17, 18, 23, 24, 31 and **15** (N. S.) No. 25. They are reproduced with general conclusions of the authors in "Wavelength Tables for Spectrum Analysis" (F. Twyman, Adam Hilger, Ltd.).

3. The results of A. de Gramont are to be found almost entirely in a long series of papers in the *Comptes Rendus*, 144 to 175. They are summarized by A. de Gramont in the *Comptes Rendus*, 171, 1106; and the table there given is also reproduced in "Wavelength Tables for Spectrum Analysis." M. le Comte A. de Gramont shortly before his death kindly read the proofs of this reproduced table, and in so doing, corrected some errors which appear in the *Comptes Rendus*.

With regard to the "raies ultimes" which are of such interest to those dealing with spectrum analysis, the following extract will be valuable:

"Considering the wide variation in the spectral sensitivity of photographic plates, the selective action of spectrographs, and other difficulties in the way of empirical determination of raies ultimes in complex spectra, the almost unfailing accuracy with which de Gramont described these must be regarded with great admiration."—*Jnl. Opt. Soc. Amer.* (May 12, 1926) 444.

4. In the catalogs of the makers, Adam Hilger, Ltd., 24, Rochester Place, Camden Road, London, N. W. 1., England.

5. For details see "Wavelength Tables for Spectrum Analysis" (Adam Hilger, Ltd.).

6. W. Gerlach: Zur Frage der richtigen Ausführung und Deutung der "Quantitativen Spektralanalyse." *Zeitschr. f. anorg. und allg. Chemie.* Band 142, Heft 3 u, 4, 387.

7. Meggers, Kiess and Stimson: Practical Spectrographic Analysis. Bureau of Standards *Scientific Paper* No. 444. (A brief review of historical matter and methods proposed for quantitative spectrographic analyses. The practical application is illustrated by work done at the Bureau with tin, gold and platinum.)

The spectrographic and chemical methods of analysis of five samples of tin are compared, and it is shown that the former method is capable of giving quantitative results of great precision. "In fact, the precision probably surpasses that of the chemical gravimetric method in a case of this kind, for it is precisely for the small quantities for which weighing errors are large that the spectral methods show their greatest sensitiveness."

8. W. Stahl: *Metall. u. Erz.* (1925) 22, 421-2.

9. W. Rosenhain: 5th Autumn Lecture to Inst. Metals (Sept. 1, 1926).

W. H. Bassett and C. H. Davis: Spectrum Analysis in an Industrial Laboratory *Trans.* (1923) 68, 662. (This article is a summary of a few instances where spectrum analysis has proved its value over a period of 8 years in the field of non-ferrous metallurgy. A large quartz spectrograph was employed, and the accessory equipment fully described. Quantitative work was not specifically attempted but it is stated that experience brings to one an increasingly clearer idea of the percentage of each element present in an unknown.)

A letter from the laboratory of Kynoch, Ltd., states that the spectrograph is being used for the examination of impurities in zinc, copper and lead with a view of passing the raw material on the basis of spectrographic examination only. They have corroborated the work on the impurities in zinc carried out by the British Non-ferrous Metals Research Association, and have done additional work on the estimation of antimony in lead.

Hull and Steele: Some Useful Applications of a Quartz Spectrograph. A. S. T. M. *Preprint* (June, 1927). (The spectrograph has been used by the authors for the examination of raw materials used in the manufacture of sheathing for underground electric cables at the plant of the General Electric Co., Schenectady, N. Y. The impurities in Babbitt metals are kept under very satisfactory control with great economy resulting from saving in the analyst's time and in inventory. In addition to this saving the accuracy of results of spectrographic examination are superior to those obtained by the average routine analyst.)

Vickers, Ltd., of River Don Works, Sheffield, in a private communication report the constant daily use for nearly 12 mo. of the spectroscope in the steel warehouse: "The operators have now reached a state of efficiency sufficiently high to detect bars of wrong quality in a batch with almost unflinching accuracy, and it is possible to state that the presence of chromium or nickel can be definitely detected when 0.1 per cent. of chromium or 0.5 per cent. nickel is present. We find it comparatively simple to differentiate by spectroscope between steels containing, for instance, the following amounts of nickel and chromium:

"(a) A carbon steel containing less than 0.5 per cent. nickel and one containing 1 per cent. nickel.

"(b) Case-hardening nickel steels containing 2, 3, or 5 per cent. of nickel.

"(c) A 3 per cent. nickel steel from a 3 per cent. nickel chrome steel.

"(d) Nickel-chrome steels containing 0.5, 1 or 1.5 per cent. chromium, respectively.

"The spectroscope is also used in this department to determine the quality of scrap selected at random from the bins of other departments, and it is found quite possible to say whether a piece of steel is carbon scrap or nickel scrap.

"We find that the time taken to carry out a spectroscopic observation is about 30 sec. to 1 min, when testing a batch of light bars of the same size and quality—heavier bars, of course, require more handling and cannot be dealt with quite so expeditiously."

The Brown-Firth Research Laboratories, Sheffield, also report the successful use of the spectroscope in distinguishing between nickel-chrome steel and chrome-vanadium steel, and state that the instrument seems to justify its adoption in the works' routine.

DISCUSSION

H. G. DE LASZLO, Cambridge, Mass. (written discussion).—I have read this paper with great interest. It is an excellent summary of recent work on the applications of the spectrograph to chemical analysis, besides giving many new data on the subject as worked out in the Hilger laboratories.

In the Spectrographic Department that has recently been opened at the Massachusetts Institute of Technology, we have had occasion to estimate platinum in silver beads in connection with the analysis of some platinum ores.⁶ Approximately the same set-up was used as described by the authors for spark spectra. Constancy of the spark source, which is of course essential to the accuracy of the method, was achieved by using a Marconi $\frac{1}{4}$ kw. field transmitter set. This set contains a converter to which is attached a rotating spark gap. The spark of the light source was in series with the moving gap. The secondary circuit was therefore broken about 600/sec. It was found that the percentage of platinum in silver could be estimated to within 10 per cent. of the total platinum present. The raies ultimes of the spark spectrum of platinum were found to be the following in International Å units, arranged in the order of sensitivity, 3064.71, 2830.29, 3204.05, 2719.02, 3042.62.

⁶ *Ind. Eng. Chem.* (1927) **19**, 1366.

Experiments are now being made on the estimation of tetra ethyl lead in gasoline. This is done by photographing the spectrum of the flame of the anti-knock gasoline when burned in a special lamp. The intensity of the lead line indicates the amount of tetra ethyl lead present.

In considering the application of spectroscopy to analysis one must not forget that a vast number of organic compounds may be recognized and estimated quantitatively, both in solution and in the state of vapor by means of their absorption spectra. Thus 1/10,000 mg. of benzol may be detected in air. This would seem to indicate that many of the fatal accidents due to benzol poisoning in rubber factories might be avoided by a spectrographic control of the air in the building.

The Production of Metallic Single Crystals

BY J. A. M. VAN LIEMPT,* EINDHOVEN, HOLLAND

(Detroit Meeting, September, 1927)

SINCE the discovery of von Laue, that a crystal forms a natural grating for X-rays, our knowledge of the structure of solids has gone forward with rapid strides. This progress is not only of purely scientific interest, but has also yielded direct technological results.

One of the most valuable results is the broadening of our knowledge of the structure of pure metals and alloys. To promote these studies it is often desirable to have at our disposal pieces of metal consisting of one single crystal.

As is so often the case in the natural sciences, we obtain the best results by making our earliest experiments on pure, simple materials and avoiding unnecessary complications. The Cryogen Laboratory at Leyden followed this method with much success, because the work was done at such low temperatures that the heat movement of the atoms was almost absent. Similarly we can simplify the studies of metals by leaving out of consideration the influence of the grain boundaries and the mutual influence of the crystals by using uniaxial instead of polycrystalline metal.

Methods of making single crystals have been scientifically studied during the past few years. Some methods were already known in the arts, but these have been improved and new methods have been developed. The methods for making metallic single crystals may be divided into the following groups:

- A. From the liquid state
- B. From the gaseous state
- C. Electrolytically
- D. By recrystallization in the solid state

METHOD A

1. *Tammann's Method*.¹—Tammann succeeded in making bismuth single crystals of a maximum length of 20 cm. by undercooling the molten metal 0.1 to 0.3° C. below its melting point in glass tubes of a maximum

* Physical chemist, Philips' Lamp Works.

¹ *Lehrbuch der Metallographie* (1923) 16; F. Stöber: *Zeitschr. für. Krist.* (1925)

diameter of 1.5 mm. By cooling the closed end somewhat a crystal nucleus was formed which absorbed the remaining liquid metal in the tube and thus formed a single crystal.

This method has been improved by Obreimow and Schubnikow,² who used tubes, drawn out to a capillary on one end, which were put vertically in a furnace. The capillary end was cooled by blowing an air current against it. In this way single crystals of bismuth, zinc, tin, antimony, magnesium, aluminum and copper were made.

2. *Czochralski's Method*.³—This much resembles the preceding method. Czochralski started with a crucible containing the molten metal at the freezing temperature. This metal was drawn upward from the crucible by means of an auxiliary wire, which moved vertically with a uniform motion. Some millimeters above the surface of the molten metal solidification started and if care was taken to keep the speed with which the auxiliary wire was drawn upward the same as the speed of crystallization, he succeeded easily in making long single crystal wires.

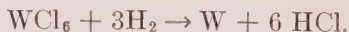
If he drew too quickly, the wire broke; if he drew too slowly, polycrystalline wires were produced. This could be proved easily by etching the surface.

In this way he could also measure the speed of crystallization in a very simple manner, the rate being about 0.2 mm. per sec. This method has been extended and improved by Gompers⁴ and Mark, Polanyi and Schmid,⁵ who made single crystals of lead, zinc, tin, aluminum, cadmium and bismuth.

METHOD B

These methods start with a single crystal, obtained according to another method. This single crystal serves as a nucleus and grows to a larger single crystal.

From the beginning of the incandescent lamp industry methods have been known for depositing tungsten metal on a glowing wire. One of these was Lodyguine's method,⁶ in which a mixture of tungsten chloride vapor (WCl_6) and H_2 strikes the glowing wire; another was that of Iseki,⁷ in which WCl_6 vapor alone strikes the glowing wire. In the first case the following reaction takes place:



In the second case the tungsten comes from the simple decomposition:



² *Zeitschr. für Physik*, (1924) **25**, 31.

³ *Zeitschr. für phys. Chem.* (1918) **92**, 219.

⁴ *Zeitschr. für Physik*, (1922) **8**, 184.

⁵ *Zeitschr. für Physik*, (1923) **12**, 60.

⁶ U. S. Patent No. 575002 and No. 575668 (1893).

⁷ Eng. Patent No. 3509 (1906).

This last reaction is reversible, WCl_6 being formed at dull red heat, and above 1500° the compound is decomposed into its elements.

1. *Koref's Method*.⁸—The first reaction mentioned was used by Koref to make a glowing tungsten single-crystal wire (Pintsch wire) grow. The wire is stretched out between two electrodes in a horizontal furnace, which is held at about 100° C. Hydrogen at a pressure of 12 mm. of Hg passes through a reservoir which leads into the furnace. The furnace contains WCl_6 , which is decomposed as described above and deposits on the incandescent wire, which has a temperature of about 1000° C. The original wire grows single crystalline. In a more recent publication, Koref, in coöperation with Fischvoigt, has stated that he succeeded in getting single crystals of molybdenum, tantalum, iron, zirconium and titanium in a similar way.⁹

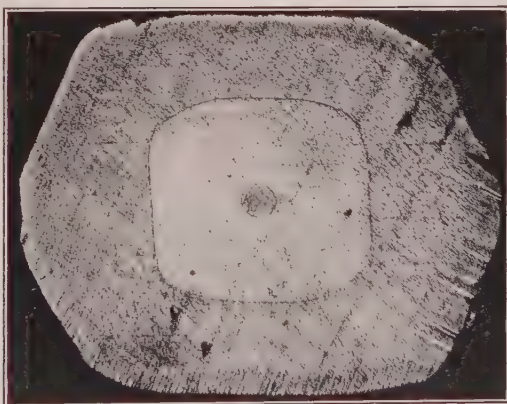


FIG. 1.—THE SMALL CIRCLE IN THE MIDDLE IS A CROSS-SECTION OF THE ORIGINAL PINTSCH WIRE. THE INNER SQUARE IS TUNGSTEN, SURROUNDED BY A LAYER OF MOLYBDENUM. ETCHANT, * $K_3Fe(CN)_6 + NaOH$. $\times 70$.

2. *Van Arkel's Method*.¹⁰—Van Arkel used the second reaction mentioned in making thin single-crystal wires grow. In this case a V-wire hanging vertically in pure WCl_6 vapor was made into a thick tungsten bar of a maximum thickness of 9 mm. at a temperature of 1600 – 1800° C. The chlorine arising from the decomposition is again converted into WCl_6 by tungsten powder, located at the bottom of the reaction vessel. The powder is held at 400° . The chlorine thus participates cyclically. Fig. 1 shows a cross-section of a single-crystal wire grown in this way. The nucleus wire may be seen distinctly, while the polygonal cross-section (the nucleus wire grows 4-, 6- or 8-sided according to the orientation of the original crystal) is certain evidence of the uniaxial nature.

⁸ *Zeitschr. für Elektr.* (1922) **28**, 511.

⁹ *Zeitschr. für techn. Physik.* (1925) 296.

¹⁰ *Physica* (1922) **2**, 56.

* 262 gm. $K_3Fe(CN)_6 + 25$ gm. NaOH in 1 l. water.

With this method we can obtain the same results with molybdenum and even produce layer-shaped single crystals of tungsten and molybdenum.¹¹

METHOD C

This method is used by the writer.¹² In this the single crystal is produced electrolytically at the surface of the metal, the latter being used as a cathode. In this way a much thicker single crystal was obtained from a small single crystal wire, which served as a cathode in a bath of molten sodium tungstate. The anode was a tungsten cylinder in the axis of which the cathode wire was placed. See Fig. 2.

METHOD D

1. *Method of Schaller and Orbig*.—This method was worked out by Schaller and Orbig when they were employed at the Pintsch Glowlamp-works in Berlin. This is a modification or adaptation of the method



FIG. 2.—PINTSCH SINGLE-CRYSTAL WIRE ELECTROLYTICALLY GROWN UP. ETCHANT,* $\text{K}_3\text{Fe}(\text{CN})_6 + \text{NaOH}$. $\times 70$.

of making pressed or squirted tungsten filaments. In this case very finely divided tungsten powder was made into a paste with a binder and was squirted into thin threads through diamond dies. Then these filaments were heated at a high temperature by means of electric current. During this process sintering takes place and the small tungsten crystals grow into larger crystals. Such wire was always polycrystalline and especially at the boundary between two crystals, which sometimes occupied the whole cross-section of the wire for a short length, and permitted displacement of one section of the filament with respect to an adjacent section, producing offsetting. This was especially noticeable on alternating current. The development of Schaller and Orbig consists in sintering so

¹¹ Geiss and v. Liempt: *Zeitschr. für Metallk.* (Aug., 1924).

¹² J. A. M. van Liempt: *Zeitschr. für Elektr.* (1925) 249. This article gives all details.

* 262 gm. $\text{K}_3\text{Fe}(\text{CN})_6 + 25$ gm. NaOH in 1 l. water.

that the small crystals grow into one. Their method is somewhat analogous to that of Czochralski. Instead of molten metal, however, there exists a microcrystalline tungsten mass. They lead the squirted and dried wire through a region of very high temperature ($2500^{\circ}\text{C}.$) with a speed equal to the speed of grain growth (up to 0.1 cm. per sec.). This hot region is obtained in a furnace with a short length of helically wound tungsten wire or by leading the squirted wire over two contacts lying near each other, and passing electric current through the squirted tungsten itself.¹³

Characteristic of the process is the fact that its success is promoted by adding a small percentage of thoria (2 per cent.) to the tungsten. ThO_2 is a highly refractory oxide, which does not even possess an appreciable vapor pressure at $2500^{\circ}\text{C}.$ The part it plays in the formation of single crystals is not known with certainty.

As we have seen, the so-called Pintsch wires, which can be made only up to a limited thickness, form the starting product for thicker single crystal bodies. Drawn tungsten wire has also been made into a single crystal wire by heating in a manner similar to that used in the Pintsch process.¹⁴

2. *Sauveur's Method*.¹⁵—As far as I know, Sauveur was the first (1912) to use the method of critical strain for the production of very large crystals. Later on several investigators successfully applied the same principle to various metals (Czochralski, Davey, Carpenter and Elam). In order to understand and explain this method, we must first explain something about deformation and recrystallization of metals in general. Deformation of metals is possible on account of the atomic planes present in the crystal; these planes can glide along each other and are therefore also called slip planes.

If, for example, we draw out a single-crystal wire, these planes are perceptible with the naked eye, because they can be formed unhindered.¹⁶ In polycrystalline material this is not the case. There the crystals hinder each other in such a way that formation of free slip planes is out of the question. We have here gliding along bent planes, so-called bent slipping. In this way, strains are produced in the crystal because the original distance of the atoms has not remained quite the same and the electron lattice has been distorted.¹⁷ The deformed metal now is in a labile condition. The lability is locally the greater as the strain increases.

¹³ German Patent 291994 (1913).

Böttger: *Zeitschr. für Elektr.* (1917) **23**, 121.

¹⁴ Goucher: Eng. Patent 174714 (1920).

¹⁵ *Metallography and Heat Treatment of Iron and Steel*, 265.

¹⁶ See Polanyi and Masing: *Ergebnisse der exakten Naturwissenschaften*, Band II,

199.

¹⁷ Geiss and van Liempt: *Zeitschr. für Metallk.* (July, 1926).

If the deformed metal now is brought to a high temperature, there will be an inclination to return again to the stable condition. Let us imagine that in a strongly deformed piece of metal there is a strain situation as represented in Fig. 3, in which case the strain either of the nucleus lattice or of the electron lattice in absolute value is expressed as a relative function of the natural distance of the atoms or valence electrons.

If we heat the places where we have a situation a , these places will become metastable and at a certain temperature change into the normal stable lattice b .

The crystal orientation of all the places b will generally be different, as they come into existence independently of each other. These extremely small crystals b now behave like a solid crystal in an under-cooled fluid and become crystallization centers for the neighboring c material. By heating at a high temperature, the metal recrystallizes,

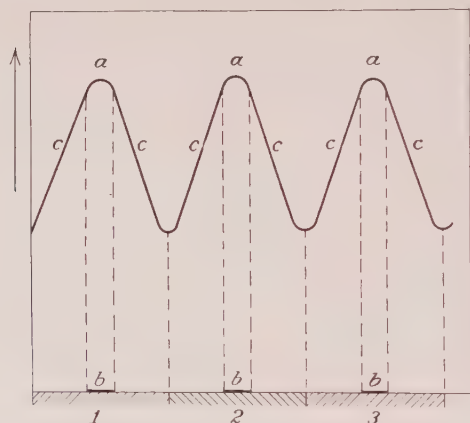


FIG. 3.—SHOWING MANNER OF RECRYSTALLIZATION IN SEVERELY COLD-WORKED METAL.

forming new crystals (Fig. 3) which in their turn may combine to form larger individuals, if heated longer or at a higher temperature. It has now been possible to determine that there exists a certain connection between the degree of deformation and the size of the crystals that exist after the recrystallization. We shall not dwell on this, as it is unnecessary for our further discussion. We shall only consider the region of the small deformations. It appears that if the degree of deformation has a certain critical (always small) value, very large crystals come into existence after recrystallization. Carpenter and Elam, for example, in this way¹⁸ found that annealed aluminum bars, which were stretched 1.6 per cent. and then heated slowly during 100 hr. from 450° to 600°, were changed into single crystals.

¹⁸ *Proc. Roy. Soc. (1921) A 100, 329.*

The explanation of this is clear if we bear in mind that, especially with small deformations, the strain situation will be different from that in severely deformed metal.

In favorably situated crystals hardly any strains will occur with small deformations whereas in unfavorably situated crystals rather strong internal strains can occur. The strain distribution is always irregular, therefore we obtain such shapes as that in Fig. 4. Here a place near *a* will become metastable at a much lower temperature than places marked *b*. Hence, if the heat is not too high and the temperature is carried up slowly, only *a* will become a nucleus and will absorb hills *b* as well as valleys *c* into a single crystal. If the metal thus deformed is heated suddenly to a much higher temperature, *a* and *b* become nuclei and the metal recrystallizes in polycrystalline form.

The method described has been applied successfully to aluminum, copper, tungsten, molybdenum and iron.

3. *Alterthum's Method*.¹⁹—In his experiments with tungsten bars, Alterthum followed quite a different procedure in obtaining large single

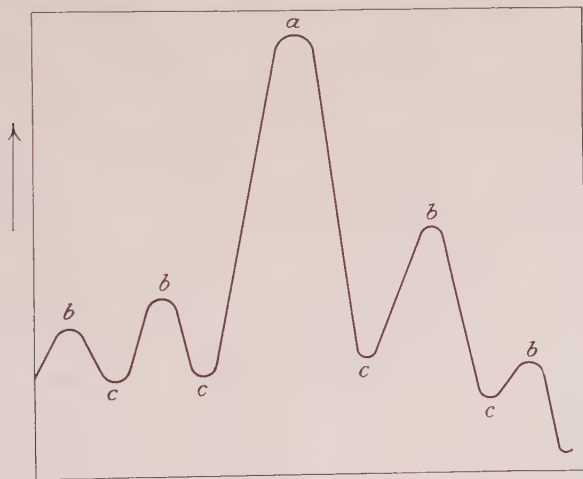


FIG. 4.—SHOWING MANNER OF DEFORMATION IN CRITICALLY STRAINED METAL.

crystals. He made use of the peculiar effect H_2O has on small tungsten crystals. For example, if we press tungsten powder into bars, sinter these and then heat them about one hour just below their melting point (3268°) in an atmosphere of moist hydrogen, these bars may grow into single crystals. This is explained by the fact that the smallest tungsten particles are oxidized by H_2O . The tungsten oxides thus formed are volatile. They deposit on the larger tungsten particles and are at the same time reduced, as the $H_2O + H_2$ mixture does not attack the big grains. Perhaps a part of the H_2 is in the atomic state.

¹⁹ *Zeitschr. für Physik. Chemie* (1924) **110**, 1.

It is understood that the above-mentioned methods, which are used by scientific investigators, are of the greatest importance for the progress of the metallographic and crystallographic sciences. Mechanism of deformation, recrystallization phenomena, conductivity, elastic properties and diffusion have been and are still being studied daily on single crystals. If knowledge is gained about single crystals, it can be utilized in the interpretation of polycrystalline material, the complex nature of which would always have remained obscure without this preliminary study.

DISCUSSION

L. W. McKEEHAN, New Haven, Conn.—What work of Czochralski's in the improvement of Sauveur's method is referred to?

S. L. HOYT, Schenectady, N. Y.—I should like to make a few additions to this very admirable summary of the methods of preparing single crystals. For instance, the work of Bridgman²⁰ in producing single crystals from the molten state by means of a mold brought to a fine point of bottom is omitted. That work is credited entirely to Tammann and the two Russians.

Secondly, a method of producing single crystals of iron was just described by Mr. McKeehan.²¹ Presumably unknown to most people, I described this method myself before the Washington Chapter of the American Society for Steel Treating,²² and it is recorded in the write-up of my lecture. The method did not receive any publicity and it is not to be wondered that Mr. McKeehan and Mr. van Liempt did not know of it. It is one that is perfectly obvious, I think, and on that account I did not stress it.

Mr. van Liempt refers to the work of Sauveur in his well-known paper of 1912. I have always been surprised that the earlier work of Charpy²³ has been neglected even by Sauveur. Charpy, in 1910, published his results in that field, showing the effect of a Brinell impression in steel in producing exaggerated grain growth and this, so far as I know, was the first time attention had been called to this method of producing grain growth by crystal strain.

I would say that neither Charpy nor Sauveur produced single crystals by this method. Subsequently Mr. Ruder,²⁴ in the research laboratory at Schenectady, produced real single crystals of silicon steel by utilizing the principles of crystal strain, a method which later on was modified by others, including Carpenter and Elam and Czochralski.

The so-called Carpenter and Elam method of producing single crystals by straining and annealing is referred to on the Continent as the Czochralski method. I thought, at first, that this term applied to Czochralski's method of fishing crys-

²⁰ P. W. Bridgman: Certain Physical Properties of Single Crystals of Tungsten, Antimony, Bismuth, Tellurium, Cadmium, Zinc and Tin. *Proc. Amer. Acad. Arts and Sci.* (1925) **60**, 305.

²¹ See page 453.

²² S. L. Hoyt: Lecture before Washington Chapter, Amer. Soc. Steel Treat. (1926) 356. (Not in the bound volume.)

²³ G. Charpy: *Rev. Mét.* (1910) **7**, 655. See also H. LeChatelier: *Rev. Mét.* (1911) **8**, 370.

²⁴ W. E. Ruder: *Trans.* (1913) **47**, 569; *Trans. Amer. Soc. Steel Treat.* (1925) **8**, 23.

tals out of the melt, but the Carpenter and Elam method is also referred to as the Czochralski method.

Z. JEFFRIES, Cleveland, Ohio.—As early as 1916 Ruder gave me a crystal of iron-silicon alloy about 14 in. long, 1 in. wide and $\frac{1}{16}$ in. thick. Ruder made a number of tests on crystals approximately this size.

Also by the method described as the Czochralski method, and the Carpenter and Elam method, Sykes produced single crystals of molybdenum about 1918. It is true that his test specimens did not consist of one single crystal but of a number of crystals comprising the full cross-section of the molybdenum wire, several of such crystals comprising the length of the test specimen. Inasmuch as fracture took place in a single crystal about halfway between the two grain boundaries, Sykes really tested single crystals of molybdenum and correctly described their properties with respect to tensile strength, reduction of area, and the wedge type of fracture.

J. A. M. VAN LIEMPT (written discussion).—Answering Mr. McKeehan, Czochralski has published two articles on the production of large and single crystals by the method of Sauveur.²⁵

The work of Sykes, mentioned by Dr. Jeffries, is known to the author, but was not mentioned because, as Dr. Jeffries pointed out, "his test specimens did not consist of one single crystal." For the same reason, the report of de Boer on zirconium crystals is omitted.²⁶

²⁵ C. Czochralski: Metallographische Untersuchungen am Zinn und ihre fundamentale Bedeutung für die Theorie der Formänderung bildsamer Metalle. *Intern. Zeitschr. für Metallk.* (1916) **8**, 1.

Verlagerungshypothese und Röntgenforschung. *Zeitschr. für Metallk.* (1923) **15**, 62.

²⁶ J. H. de Boer and J. D. Fast: Über die Darstellung der reinen Metalle der Titangruppe durch thermische Zersetzung ihrer Jodide. *Zeitschr. anorg. und allgem. Chem.* (1926) **153**, 1.

Ternary Systems of Lead-antimony and a Third Constituent*

By R. A. MORGEN, L. G. SWENSON, F. C. NIX AND E. H. ROBERTS, CHICAGO, ILL.

(New York Meeting, February, 1928)

THE binary system lead-antimony has been the subject of comprehensive investigations in these laboratories by Dean¹ and his associates. The effect of a third constituent on this system, particularly on the lead-rich alloys in which dispersion hardening was found, has a commercial value as well as an academic interest. This paper covers the effect of the addition of copper, bismuth and tin, all of which are likely to be found in commercial lead-antimony alloys, and is divided into three parts, as follows:

- I. The System Lead-Antimony-Copper
- II. The System Lead-Antimony-Bismuth
- III. The Lead Corner of the System Lead-Antimony-Tin

These three systems are of three different types, and hence may be considered as covering three general kinds of additions. Bismuth forms no compounds with either lead or antimony and forms solid solutions with both. Copper forms several compounds with antimony as well as solid solutions but with lead it forms a two liquid layer system and no appreciable solid solution. Tin is soluble in both lead and antimony in the solid state and also forms a compound with antimony. The effect of small amounts of bismuth on the lead-antimony alloys is small, having no appreciable effect on the solubility of antimony. The temperature of the solidus floor is lowered appreciably by the presence of bismuth, cutting down the range of heat treatment. Copper, on the other hand, due to compound formation, increases the apparent solubility of antimony. The excess antimony is tied up with the copper finally and so is not available for dispersion hardening. The net result of addition of small amounts of copper is to shift the dispersion hardening peak of the

* Contribution from the Manufacturing Development Branch, Hawthorne Works, Western Electric Co.

¹ R. S. Dean: The System Lead-antimony. *Jnl. Am. Chem. Soc.* (1923) **45**, 1683.

R. S. Dean, W. E. Hudson and M. F. Fogler: The System Lead-antimony. *Ind. & Eng. Chem.* (1925) **17**, 1246.

R. S. Dean and W. E. Hudson: Grain Growth in Lead Containing One Per Cent. of Antimony. *Jnl. Am. Chem. Soc.* (1924) **46**, 1778.

R. S. Dean, L. Zickrick and F. C. Nix: The Lead-antimony System and Hardening of Lead Alloys. *Trans.* (1926) **73**, 505.

lead-antimony alloys to a higher antimony content. Tin has a deleterious effect on the dispersion hardening of lead-antimony alloys. Although the addition of tin does not change the solubility of antimony at high temperatures appreciably, it has a tendency to hold it in solution at room temperature, thus cutting down the amount of antimony available for hardening. At the same time, the solidus floor is lowered, shortening the range of heat treatment.

The System Lead-antimony-copper

BY RALPH A. MORGEN, FOSTER C. NIX AND LESLIE G. SWENSON

The only previous work on this system, which has come to our attention, was done by H. Schack,² who made an investigation of the interior of the diagram. He used microscopic data and some cooling curves, so that he obtained the general direction of the isotherms and the outline of the two liquid layer surfaces. Since, for purposes of cable-sheath manufacture, leads containing copper are used, it is important to know the effect of copper. It was, therefore, thought advisable to supplement Schack's results with further data, especially near the lead end of the diagram.

The three binary systems which form the outline of the ternary diagram are rather well known. The system lead-antimony has been extensively investigated in these laboratories.³ In a recent work, Schumacher and Nix⁴ checked the solidus line very accurately. With the use of a magnetic method, Endo⁵ has given evidence for a solid solubility of lead in antimony of 5 per cent. by weight. The system copper-antimony has been investigated by H. C. H. Carpenter,⁶ H. Reimann,⁷ N. S. Kournakoff and K. F. Beloglasoff.⁸ Three compounds, Cu_5Sb_2 , Cu_3Sb and Cu_2Sb are formed; Cu_5Sb_2 breaks down into the other two on cooling. Antimony forms a solid solution with copper up to 8 per cent. by weight, and Endo⁹ has shown that copper forms a solid solution with antimony up to 1.4 per cent. The system copper-

² H. Schack: Das ternäre System Kupfer Blei-Antimon. *Zeitschr. anorg. Chem.* (1923) **132**, 265.

³ R. S. Dean: *Op. cit.*

⁴ E. E. Schumacher and F. C. Nix: The Solidus Line in the Lead-antimony System. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 195.

⁵ H. Endo: On the Relation between the Equilibrium Diagram, Etc. *Sci. Repts. Tohoku Imp. Univ. (Sendai)* (1925) **14**, 503.

⁶ H. C. H. Carpenter: The Copper-antimony Equilibrium. *Intern. Zeitschr. Met.* (1913) **4**, 300.

⁷ H. Reimann: *Zeitschr. Metallkunde.* (1920) **12**, 321.

⁸ N. S. Kournakoff and K. F. Beloglasoff: Des composés de cuivre et d'antimoine. *Rev. Metal.* (1922) **19**, 588.

⁹ H. Endo: *Loc. cit.*

lead brings in complications due to the formation of two liquid layers. This system has been considered by Friedrich.¹⁰

EXPERIMENTAL PROCEDURE

The materials used were Doe Run lead, a desilverized Southeastern Missouri product, Chinese antimony analyzing 99.65 per cent. antimony, and electrolytic copper of 99.94 per cent. purity. Melts were made in a graphite crucible heated in an electric furnace. Many of the compositions were checked analytically but in no case was an appreciable difference found from the calculated amounts.

TABLE 1.—*Cooling-curve Breaks*

Composition			Breaks,* Degrees Centigrade
Cu, Per Cent.	Sb, Per Cent.	Pb, Per Cent.	
5	5	90	627, 428, 272, 252
5	10	85	629, 490, 284
5	13	82	609, 273, 254
5	16	79	588, 521, 252
5	40	55	474, 410, 252
5	50	45	438, 248
5	60	35	480, 446, 246
5	80	15	527, 460, 246
10	10	80	628, 460, 310, 250
10	13	77	630, 481, 400, 288, 250
10	20	70	630, 285, 251
10	30	60	546, 534, 338, 250
10	40	50	517, 490, 402, 393, 251
10	50	40	485, 434, 251
10	60	30	468, (practically flat), † 251
10	70	20	503, 479, 251
10	80	10	530, 485, 248
20	10	70	610, 428, 416, 321
20	30	50	610, 530, 304, 250
20	50	30	540, 440, 251
20	70	10	498, 493, 251
20	75	5	504, (practically flat), 251
2	5	93	300, 247
2	10	88	268, 250
2	13	85	247, (flat)

* More than three breaks occur in the two-liquid-layer region where it was not possible to always maintain equilibrium between the two layers.

† "Practically flat" indicates the simultaneous separation of two solids giving a larger break.

¹⁰ K. Friedrich: Untersuchungen über Schichten bildende Systeme. *Met. u. Erz.* (1913) 10, 575; *Metall.* (1907) 4, 300.

The cooling curves were made with the aid of a chromel-alumel thermocouple, protected by a silica tube. The curves were drawn by a Leeds and Northrup recording potentiometer. The potentiometer and

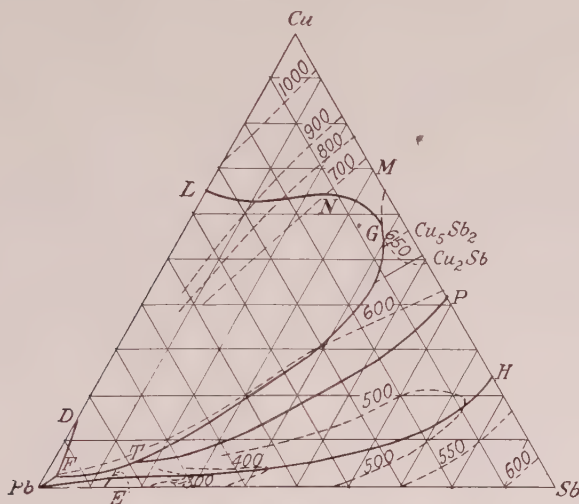


FIG. 1.—DIAGRAM OF SYSTEM COPPER-LEAD-ANTIMONY.



FIG. 2.—PLASTER MODEL OF SYSTEM COPPER-LEAD-ANTIMONY.

thermocouple were calibrated using the melting points of tin, lead, zinc and aluminum. After complete solidification, the melts were cut longitudinally and investigated for evidence of two liquid layers. Photomicrographs were taken to give the shape and type of crystallization

that had taken place. Table 1 gives the typical cooling-curve data on the melts made near the Pb-Sb line and in the vicinity of the lead corner.

EXTENT OF THE MISCIBILITY GAP

The ternary diagram of the system is given in Fig. 1. Fig. 2 is a photograph of a plaster model of the system. The shaded surface represents the two-liquid-layer region. Such a model is beneficial in visualizing the contours of the system. The shape of the projection of the shaded surface, *DFTGL*, has important practical applications in that it determines which alloys may be used to get a homogeneous mass. Table 2 gives the composition of melts used to locate the extent of the two-liquid-layer system. Usually the existence of two liquid layers could be seen macroscopically in the frozen melt, but in doubtful cases, close to the line, the microscope was used.

TABLE 2.—Location of Areas of Two Liquid Layers

Melt No.	Cu, Per Cent.	Sb, Per Cent.	Pb, Per Cent.	No. of Liquid Layers
5	5	10	85	2
101	5	5	90	2
9	5	15	80	On Boundary
*1	10	10	80	2
14	10	20	70	On Boundary
15	15	20	65	2
17	15	25	60	On Boundary
*20	18	22	60	2
16	20	20	60	2
68	20	30	50	On Boundary
18	25	30	45	2
63	30	40	30	1
*3	30	30	40	2
*16	35	35	30	2
*11	40	30	30	2
64	40	35	25	2
69	40	40	20	On Boundary
*10	50	20	30	2
*12	50	25	25	2
*17	50	30	20	2
79	55	30	15	2
80	55	35	10	2
*3	60	10	30	2
78	60	20	20	2
*60	60	20	20	2
75	60	25	15	2
81	60	35	5	1
77	65	15	20	1
76	65	25	10	On Boundary

* Schack's values.

The point F occurs at about 2.5 per cent., or the limit of solid solubility of antimony, in lead. The direction of DF is almost perpendicular to the Pb-Sb line. At F there is a sharp break, the curve remaining almost horizontal to T and then describing a wide curve to G , which is very near the Cu_5Sb_2 line. The miscibility gap does not cross the 5 per cent. Pb line, which is in accordance with the observation of Endo¹¹ that lead is soluble in solid antimony up to 5 per cent. lead. Up to this concentration of lead, the properties of the liquid are very similar to pure

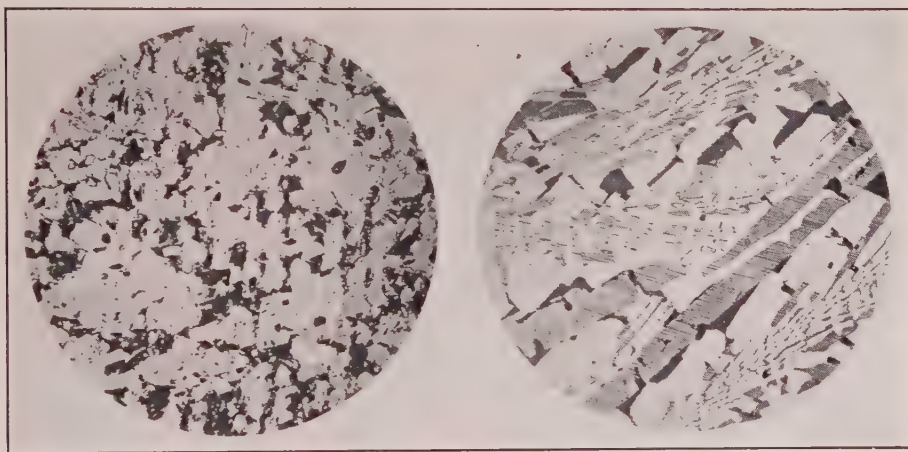


FIG. 3.

FIG. 4.

FIG. 3.—MELT 63 (30 PER CENT. Pb, 40 PER CENT. Sb, 30 PER CENT. Cu) SHOWS ROUNDED PARTICLES OF Cu_3Sb RESULTING FROM DECOMPOSITION OF Cu_5Sb_2 . $\times 100$.

FIG. 4.—MELT 26 (10 PER CENT. Pb, 70 PER CENT. Sb, 20 PER CENT. Cu); PRIMARY Cu_2Sb APPEARS AS DARK NEEDLES. $\times 100$.

Reduced to $\frac{2}{3}$ original size.

antimony. From G the miscibility gap curve returns to the Cu-Pb axis rather sharply at L . This is to be expected because in this region, in the liquid state, practically all the antimony is tied up as Cu_5Sb_2 , and so the system to be considered is Cu_5Sb_2 , Pb, Cu.

GENERAL FEATURES OF SINGLE LIQUID PHASE PORTIONS

The location of the areas in which different constituents separated as primary crystals will now be considered. The area Cu-LNM represents the primary crystallization of the solid solution of antimony in copper. In the area $MNG\text{-Cu}_5\text{Sb}_2$, the primary crystals are solid solution of copper in Cu_5Sb_2 . This breaks down on cooling, giving Cu_3Sb and Cu_2Sb . $\text{Cu}_5\text{Sb}_2\text{-GTP}$ encloses the area in which Cu_5Sb_2 separates, which decom-

¹¹ H. Endo; *Loc. cit.*

poses on cooling to Cu_3Sb and Cu_2Sb . The line TP is a peritectic line, on one side of which Cu_2Sb is found in rounded particles as the result of decomposition of Cu_5Sb_2 , and on the other side Cu_2Sb is found in needles as the primary crystal. This is illustrated by the photomicrographs of melts 63 and 26 (Figs. 3 and 4). The line HE represents the limit of the appearance of primary Cu_2Sb ; *i. e.*, the binary eutectic line, Cu_2Sb - Sb , the area HE - Sb separating solid solutions of copper or lead or

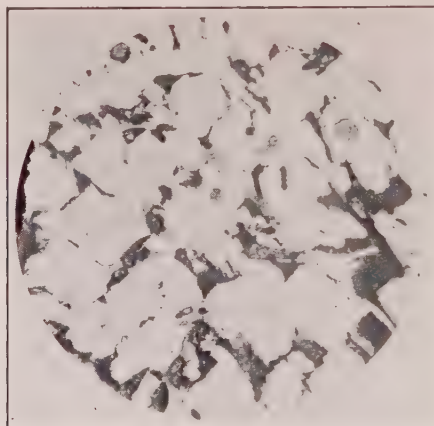


FIG. 5.—MELT 22-A (10 PER CENT. Pb , 80 PER CENT. Sb , 10 PER CENT. Cu); PRIMARY LIGHT CRYSTALS OF Sb SOLID SOLUTION. $\times 100$.

Reduced to $\frac{2}{3}$ original size.

both in antimony. E represents the ternary eutectic of a composition containing less than 2 per cent. Cu , and lead and antimony in the proportion in which they exist in the lead-antimony eutectic and at approximately the same temperature, 247°C . No difference in the cooling curves could be detected between zero per cent. and 2 per cent. copper when lead and antimony were present in the proportions in which they exist in the binary eutectic.

LOCATION OF LINE HE

Since the point H represents the eutectic point between Cu_2Sb and Sb , there should be a valley connecting it to the ternary eutectic E . This is represented by the line HE . In order to locate some definite points on this line, sectional diagrams of the liquidus surface at 5, 10 and 20 per cent. copper were drawn. The values were taken from Table 1. The 5 per cent. line shows a low point at 50 per cent. Sb . The 10 per cent. section has its minimum at 60 per cent. Sb and the line HE is cut at 75 per cent. Sb by the 20 per cent. minimum point. Where these sectional diagrams cut the two liquid layer areas, there are often more than three breaks in the cooling curves. Ordinarily, the first change of

slope occurs on the precipitation of a single solid in equilibrium with the liquid, the second when two solids are in equilibrium with the liquid, and finally the invariant point where three solids and the liquid are in equilibrium. In a two-liquid-layer system, it is seldom possible to cool slowly enough to maintain equilibrium between the two liquid layers, so the number of breaks is not so significant.

The position of the line *HE* obtained from these data was confirmed microscopically. On one side of the line the needle-like structure of primary Cu_2Sb is easily identified (Fig. 4). On the other side of the line, white crystals of solid solution of lead or copper in antimony may be identified as the primary constituent (Fig. 5). Table 3 gives the result of this microscopic evidence.

TABLE 3.—*Location Line HE*

No. of Sample	Cu, Per Cent.	Sb, Per Cent.	Pb, Per Cent.	Type of Primary Crystal*
34	5	60	35	Sb
28	5	65	30	Sb
23	5	70	25	Sb
19	5	75	20	Sb
35	10	60	30	Ground Mass Sb and Cu_2Sb
29	10	65	25	Sb
24	10	70	20	Sb
36	15	60	25	Cu_2Sb
30	15	65	20	Cu_2Sb
25	15	70	15	Cu_2Sb
21	15	85	10	Cu_2Sb
31	20	65	15	Cu_2Sb
26	20	70	10	Cu_2Sb

* Cu_2Sb : primary needles, dark color; Sb: solid solution of Pb or Cu in Sb, jagged white particles.

That the line *HE* dips toward the Pb-Sb axis is demonstrated by the series of photomicrographs in Fig. 6. Melt 89 of the binary eutectic Cu_2Sb -Sb shows the characteristic fine-grain eutectic structure. On addition of small amounts of lead, the needle-like primary crystals of Cu_2Sb appear, being distinct when only 0.5 per cent. lead is added.

THE PERITECTIC LINE, PT

As noted under the general comments, the peritectic line was located microscopically in a manner similar to the location of *HE*. On one side of the line, Cu_3Sb_2 is the primary crystal which, on cooling, breaks down into distinctly rounded particles of Cu_2Sb , while on the other side needles of Cu_2Sb are found (Figs. 3 and 4). The melts and their compositions are given in Table 4.

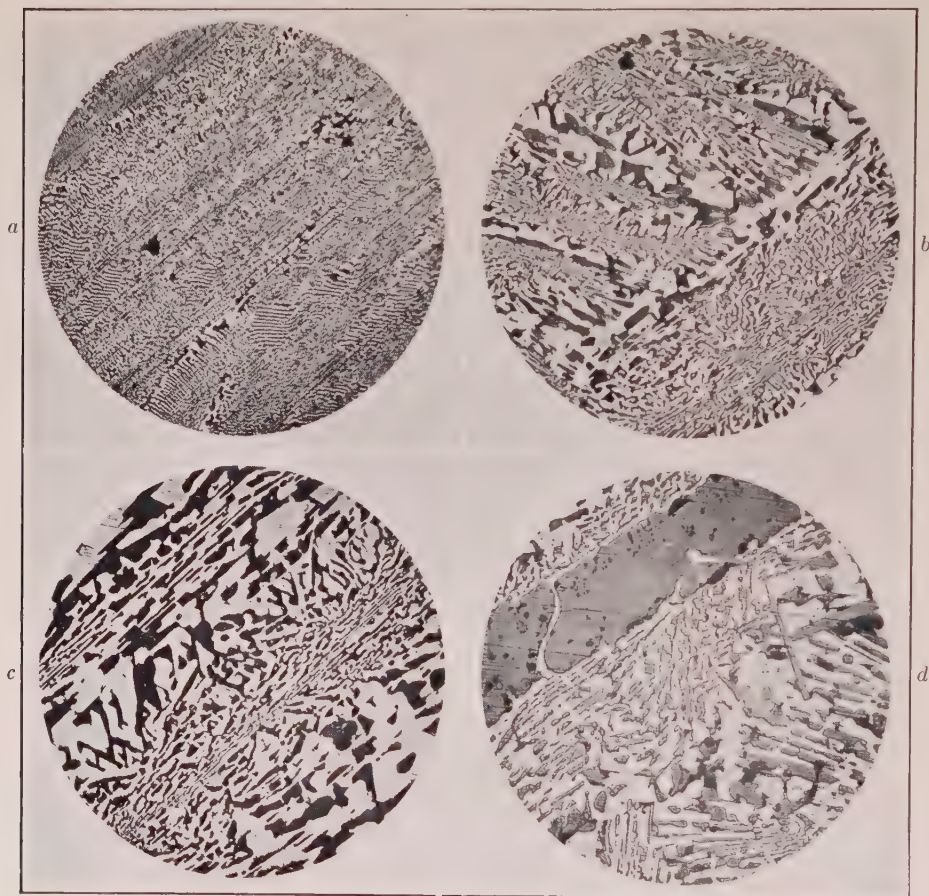


FIG. 6.—PRIMARY Cu_2Sb NEEDLES ON ADDITION OF Pb TO Cu_2Sb -Sb EUTECTIC. *a*, MELT 89; BINARY EUTECTIC Cu_2Sb -Sb. $\times 100$. *b*, MELT 90; BINARY EUTECTIC Cu_2Sb -Sb PLUS 0.5 PER CENT. Pb. $\times 100$. *c*, MELT 91; BINARY EUTECTIC Cu_2Sb -Sb PLUS 1.0 PER CENT. Pb. $\times 100$. *d*, MELT 92; BINARY EUTECTIC Cu_2Sb -Sb PLUS 5.0 PER CENT. Pb. $\times 100$.

Reduced to $\frac{2}{3}$ original size.

TABLE 4.—*Location of the Peritectic Line*

No. of Sample	Cu, Per Cent.	Sb, Per Cent.	Pb, Per Cent.	Type Crystal*
13	5	20	75	N
67	10	30	60	R. P. and N
61	30	50	20	R. P.
39	30	60	10	N
66	35	55	10	R. P. and N

* N, needles. R. P., rounded particles.

THE PSEUDOBINARY LINE— $\text{Cu}_2\text{Sb-Pb}$

Schack¹² showed that the line $\text{Cu}_2\text{Sb-Pb}$ started, from the Cu_2Sb side, to be a pseudobinary line, but on striking the two-liquid-layer regions, it lost its identity as such. If this line is truly pseudobinary, *i. e.*, mixtures of lead with copper and antimony in the ratio 2 mol Cu to 1 mol Sb, the line should reappear in the lead corner of the diagram. If a eutectic between Pb and Cu_2Sb should exist, it would contain only small amounts of Cu_2Sb . In an attempt to locate such a point, Morgen¹³ showed analyt-

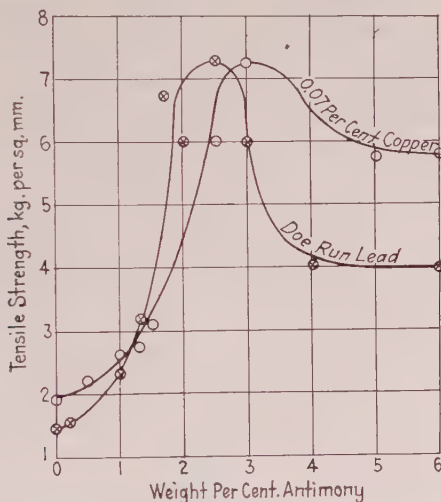


FIG. 7.—EFFECT OF COPPER ON TENSILE STRENGTH OF LEAD-ANTIMONY ALLOYS; NOTE SHIFTING OF PEAK TO HIGHER ANTIMONY CONTENT DUE TO PRESENCE OF COPPER.

ically and microscopically that the line is not directed exactly toward the lead corner but is shifted by the formation of the lead-antimony solid solution. Therefore, on this line the primary crystals, close to the lead end, are solid solution of antimony in lead. No Cu_2Sb appears as such, but the copper crystallizes as pure copper or Cu_3Sb .

EFFECT OF COPPER ON SOLID SOLUBILITY OF ANTIMONY IN LEAD

The presence of small amounts of copper has a tendency to increase somewhat the solid solubility of antimony in lead, at least at the higher temperatures. Traces of copper of the order of 0.02 per cent. by weight seem to have just as much effect as 0.1 or 0.2 per cent. This would indicate that the solid solubility of copper in lead-antimony alloys was of the order of magnitude of 0.02 per cent. The values obtained by

¹² H. Schack: *Loc. cit.*

¹³ R. A. Morgen: The Relation between Pseudobinary Lines and Solid Solutions in Metallic Ternary Systems. *Jnl. Am. Chem. Soc.* (1927) **49**, 39.

conductivity data are given in Table 5. As a consequence of this solubility, small amounts of copper have the effect of shifting the dispersion hardness peak of lead-antimony alloys toward a higher antimony con-

TABLE 5.—*Effect of Copper on Solid Solubility of Antimony in Lead**

Temperature, Degrees Centigrade	0.00 Per Cent. Cu Per Cent. Sb	0.02 Per Cent. Cu Per Cent. Sb	0.07 Per Cent. Cu Per Cent. Sb	0.10 Per Cent. Cu Per Cent. Sb	0.20 Per Cent. Cu Per Cent. Sb
180	1.25				
200	1.36			1.54	1.70
220		2.49			2.35
225				2.37	
238	2.05	2.73		2.69	2.76
247†	2.45†		2.81†		

* These data were taken from laboratory records and include the work of W. E. Hudson, M. F. Fogler, and E. J. Quinn.

† Thermal data.

tent. While there is no absolute increase in the dispersion hardness of the alloys, there is a change in the location of the maximum as shown in Fig. 7.

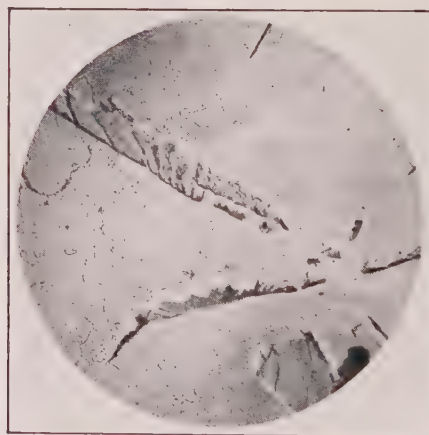


FIG. 8.—98.95 PER CENT. Pb, 1 PER CENT. Sb, 0.05 PER CENT. Cu. PRIMARY BLUE-VIOLET Cu_2Sb APPEARS AS DARK NEEDLES. $\times 400$.

This photomicrograph was obtained with an acetic acid etch and the method of cutting developed by F. F. Lucas.¹⁴

Reduced to $\frac{2}{3}$ original size.

The effect of copper in the lead corner can be summed up in the statement that lead-antimony alloys of the compositions corresponding to those which form solid solutions act like pure lead toward *small* amounts

¹⁴ F. F. Lucas: Application of Microtome Methods to the Preparation of Soft Metals for Microscopic Examination. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 481.

of added copper. Therefore, the pseudobinary line is not $\text{Cu}_2\text{Sb-Pb}$ but Cu_2Sb -solid solution of Sb in Pb. In attempting to find just where the Cu_2Sb line cuts the Pb-Sb axis, a melt was made up containing 1 per cent. Sb and 0.05 per cent. Cu. This corresponds to ordinary cable sheath. In this case almost all the copper appears in the form of Cu_2Sb , but most of it comes out of the last part that crystallizes. Samples taken from the edge of the solidified sample showed only isolated crystals of Cu_2Sb , while in the center, where the last traces of liquid solidified, definite crystals of Cu_2Sb could be seen (Fig. 8). The $\text{Cu}_2\text{Sb-Pb}$ solid-solution line, therefore, hits the Pb-Sb axis somewhere between 0.05 per cent. and 1.0 per cent. Sb.

The role of copper in the lead-antimony alloys is then that of a competitor with lead for antimony. We may either get lead-antimony solid solution and pure copper (some Cu_2Sb) or else copper antimonide and lead. Any mixture in between may be obtained by proper control of concentrations. The separating constituents depend on the partial free energies in a lead solution of copper, copper antimonide and antimony. Very small amounts of copper (less than 0.1 per cent.) act toward the lead-antimony solution as if an additional amount of lead were added, giving an increased solubility of antimony. However, this increased antimony content is not available for dispersion hardening and so only shifts the point of maximum hardness toward a higher antimony content.

SUMMARY

1. Further data have been obtained on the system copper-lead-antimony and a diagram drawn from the data available to date.
2. The boundary of the miscibility gap has been more accurately plotted.
3. A relation between solid-solution formation and the existence of a pseudobinary line has been pointed out.
4. The presence of copper shifts the point of maximum hardness in dispersion hardened lead-antimony alloys toward a higher antimony content.

The System Lead-antimony-bismuth

BY RALPH A. MORGEN, FOSTER C. NIX AND EVELYN H. ROBERTS

The ternary system lead-antimony-bismuth, although based on three rather well known binary systems, has not been studied, so far as we are aware. The lead-antimony equilibrium is well known. The latest work on this system has been done by Dean¹⁵ and his associates and by Endo.¹⁶

¹⁵ R. S. Dean: The System Lead-antimony. *Jnl. Am. Chem. Soc.* (1923) **45**, 1683.

R. S. Dean, L. Zickrick and F. C. Nix: *Op. cit.*

¹⁶ H. Endo: *Op. cit.*

The system lead-bismuth has been rather extensively studied by Stoffel,¹⁷ Barlow,¹⁸ Herold,¹⁹ and Endo.²⁰ All investigators have agreed that the system is a simple eutectiferous one with the eutectic mixture freezing at 120° C. and containing 43 per cent. bismuth, 57 per cent. lead. However, there has been disagreement as to the extent of the solid solutions at both ends. Barlow²¹ says that the solid solubility of bismuth in lead is between 30 and 36 per cent. From cooling-curve data the value seems to be about 34 per cent. Lead has a smaller solubility in bismuth, only 1.0 per cent. at the eutectic temperature according to Barlow. Endo,²² however, finds 4 per cent. lead soluble in bismuth.

Alloys of antimony and bismuth have not had the commercial importance of those of the other two parts of this ternary system. As a result, this system is not as well known as the others. Huttner and Tammann²³ show a break in the curve at 50 per cent. by weight of each substance. This work has been repeated by Cook,²⁴ who fails to find the break. The diagram as given by Cook is used as our base.

From these three binary diagrams it will be seen that the liquidus surface of the ternary diagram is comparatively simple. As there are no binary compounds, a ternary compound is hardly to be expected. The high points on the diagram are on the antimony-bismuth binary line, sloping off toward the lines joining the lead-antimony, lead-bismuth eutectics, with the ternary eutectic. As no compounds are formed in the system, the addition of bismuth to a lead-antimony alloy should decrease the solubility of antimony in lead, and the addition of antimony to lead-bismuth mixtures should behave similarly. Since bismuth is almost twenty times as soluble in solid lead as antimony, the addition of antimony to lead-bismuth should have much more effect on decreasing the solubility of bismuth than in the reverse case. These assumptions are borne out in the conductivity data which follow.

EXPERIMENTAL RESULTS

The liquidus and part of the solidus surfaces were obtained by means of cooling curves. The materials used were Doe Run lead, purified

¹⁷ A. Stoffel: Untersuchungen über binäre und ternäre Legierungen von Zinn, Blei Wismut und Cadmium. *Zeitschr. anorg. Chem.* (1907) **53**, 150.

¹⁸ W. E. Barlow: The Binary and Ternary Alloys of Cadmium, Bismuth and Lead. *Jnl. Am. Chem. Soc.* (1910) **32**, 1394.

¹⁹ W. Herold: Das binäre System Blei-Wismut. *Zeitschr. anorg. Chem.* (1920) **112**, 131.

²⁰ H. Endo: *Op. cit.*

²¹ W. E. Barlow: *Loc. cit.*

²² H. Endo: *Loc. cit.*

²³ K. Huttner and G. Tammann. Über die Legierungen des Antimons und Wismuts. *Zeitschr. anorg. Chem.* (1905) **44**, 138.

²⁴ M. Cook: The Antimony-bismuth System. *Jnl. Inst. Met.* (1922) **28**, 421.

bismuth, and the best grade of Chinese antimony. The melts were made up synthetically and then certain ones, picked at random, were analyzed. The analysis in all cases checked within the experimental error.

The system was then built from a series of profiles, made by holding one of the three constituents constant and varying the other two. In most cases the profiles were made with constant amounts of bismuth. Table 6 gives the breaks in the cooling curves for the 10, 20, 30, and 60

TABLE 6.—*Breaks in Cooling Curves of Lead-antimony-bismuth Melts*

Per Cent. Pb	Per Cent. Sb	Per Cent. Bi	Breaks, Deg. C.
20	70	10	566*
30	60	10	543*
40	50	10	493, 210*
50	40	10	449, 204*
70	20	10	316, 204*
80	10	10	217*
70	10	20	193*
60	20	20	341, 193*
50	30	20	413, 183*
40	40	20	463, 182*
30	50	20	510, 118
20	60	20	542, 125
10	70	20	510, 125
50	20	30	360, 123
40	30	30	424, 149*
30	40	30	471, 121
20	50	30	516, 122
35	5	60	214, 120
27.5	12.5	60	313, 122
20	20	60	349, 121
10	30	60	466, 125
5	35	60	477, 127

* All melts so marked seemed to have a break in the vicinity of 120°; but were cooling so slowly that the exact temperature of the break could not be obtained.

per cent. constant amounts of bismuth. The ternary eutectic is very near that of the binary eutectic between lead and bismuth containing less than 1 per cent. antimony.

It is interesting to note that in many cases there is only one break in the curves (outside of the slight one at the ternary eutectic). This is explained by the primary precipitation of a ternary solid solution rich in antimony so that the remaining liquid tends toward the composition of the ternary eutectic. The profile curves give a clue as to the boundaries

of the liquid composition from which the saturated ternary solution separates. The appearance of the second break before the ternary eutectic point indicates that the liquid composition is no longer changing composition along a line directed towards the ternary eutectic. Fig. 9

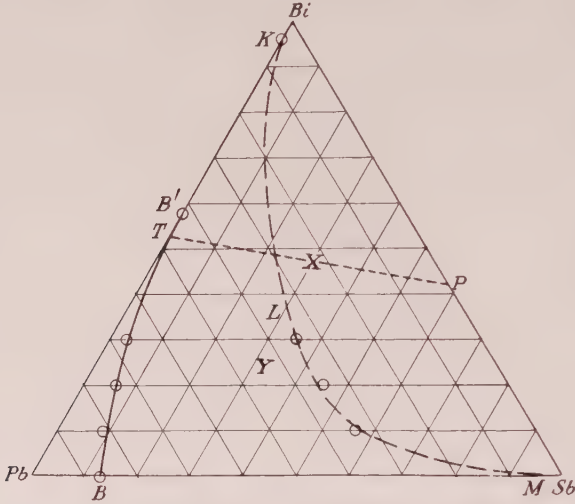


FIG. 9.—SYSTEM LEAD-ANTIMONY-BISMUTH.



FIG. 10.—PLASTER MODEL OF SYSTEM LEAD-ANTIMONY-BISMUTH.

represents a projection of the ternary system. The line *KLM* shows the boundary of the region from which the ternary solid solution separates and the remaining liquid changes composition on a line directed towards the ternary eutectic point. That is, a melt of composition *X* on cooling

would drop out as solid solution, compositions along XP and the remaining liquid changes along XT . A melt of the composition Y , on the other hand, precipitates the saturated ternary solutions as primary crystals and the liquid changes composition in such a way as to hit somewhere along the line BT , giving the second break, then it changes along this line to the ternary eutectic T . No attempt was made to find the solid solutions in the antimony, bismuth part of the diagram. A plaster model of the ternary system is shown in Fig. 10. The valley connects the lead-antimony and lead-bismuth eutectics with the ternary eutectic which is very close to the lead-bismuth eutectic. There is no eutectic between antimony and bismuth so that the side slopes down in an unbroken sweep towards this valley.

SOLID-SOLUTION RANGE

The solid solutions in the lead corner of the diagram were of particular interest to us. The change of conductivity of the alloys with composition at constant temperature was used to measure the solid solubility. In general, the addition of a substance which forms a solid solution causes a much more marked drop in the conductivity of a metal than one which does not form a solid solution. Therefore, the addition of the solute substance beyond the limit of solid solubility causes a break in the conductivity-composition curve. This method has been used successfully in the study of binary systems, and it is also applicable to ternary systems. If the amount of one of the substances is fixed, the solid solubility of the other two in the presence of this constant amount of third constituent may be obtained by the method outlined above.

EXPERIMENTAL RESULTS

The experimental set-up was a slight modification of the ordinary potential drop method. The room temperature values were obtained on straight pieces of wire suspended between knife edges. The 100° C. values were obtained by winding the wire on an alundum cylinder and immersing in a thermostatically controlled crisco bath.

The first series of experiments were designed to study the effect of small amounts of bismuth on the solid solubility of antimony. Alloys containing varying amounts of antimony and a constant 1 per cent. of bismuth were measured. The results are tabulated in Table 7 and plotted in Fig. 11. From these results it is evident that there is little change of solubility of the antimony between 100° and 25° C. in the presence of 1 per cent. bismuth. The addition of the first few tenths per cent. of antimony lowers the conductivity of the lead by formation of lead-antimony solid solution. At about 0.5 per cent. antimony the lead becomes saturated with antimony, then further addition of antimony

TABLE 7.—*Conductivity of the 1 Per Cent. Bismuth-lead-antimony Series in Mhos per Gram-meter*

Per Cent. Bi	Per Cent. Sb	Conductivity, 25° C.	Conductivity, 100° C.
1.0	0.0	0.40600*	0.30800*
1.0	0.5	0.38229	0.29643
1.08	0.94	0.37645	0.29864
1.0	1.5	0.37664	0.29599
1.01	2.11	0.38628	0.30099
1.0	2.5	0.37950	0.29840
1.08	2.98	0.38553	0.29993
1.0	4.0	0.38180	0.29761
1.04	4.75		0.29593
1.0	8.0	0.36151	0.28696
1.0	12.0	0.34244	0.27425

* Extrapolated value from lead-bismuth data of Herold and of Barlow.

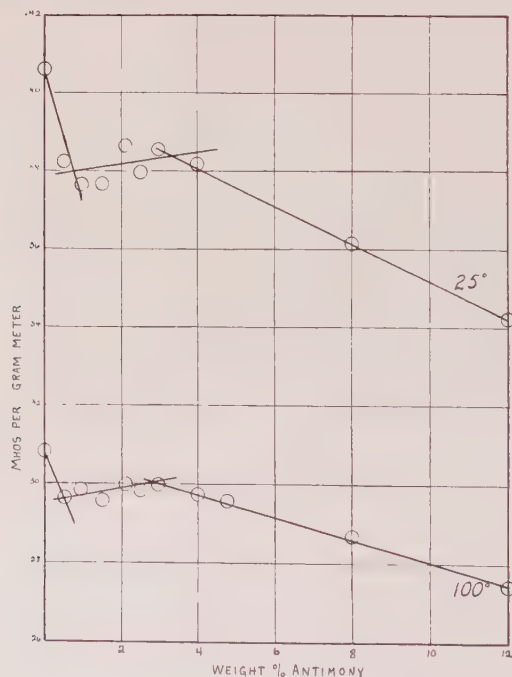


FIG. 11.—CONDUCTIVITY AT 25° AND 100° C. OF 1 PER CENT. BISMUTH-LEAD-ANTIMONY SERIES.

removes the bismuth from solid solution. During this period there is a slight increase in the conductivity. By the time 2.5 per cent. antimony has been added, there is an appreciable decrease in the conductivity caused by the presence of enough antimony-bismuth solid solution.

The course of the solid solubility along the 1 per cent. bismuth line, at higher temperatures, was traced by means of a series of hardening experiments. This group of alloys was annealed at 225° C. and then quenched in water. The alloy which showed the maximum increase of hardness with age represents the limit of solid solubility at the temperature from which it was quenched. These results (Table 8) show that the presence of 1 per cent. bismuth has little effect on the solubility of antimony in lead up to 225° C.

TABLE 8.—*Tensile Strength of 1 Per Cent. Bismuth-lead-antimony in Kilograms per Square Millimeter*

Per Cent. Bi	Per Cent. Sb	Quenched from 225° C.	Aged 72 Hr. at 20°	Aged 120 Hr. at 20°	Aged 72 Hr. at 50°	Aged 120 Hr. at 50°
1	0.5	2.092	1.974	2.075	3.437	2.053
1	1.5	2.446	3.16	3.538	4.415	4.42
1	2.0	3.04	5.29	5.605	5.605	5.43
1	2.5	3.395	5.72	5.94	5.72	5.49
1	3.0	3.830	4.185	4.54	5.25	5.13
1	4.0	3.395	3.592	3.87	4.065	4.065
1	5.0	3.476	3.79	3.945	3.900	4.09
1	6.0	3.636	3.828	3.908	3.635	3.89
1	8.0	4.185	4.38	4.5	4.345	4.46
1	12.0	4.540	4.50	4.56	4.46	4.56

A second series of conductivity experiments was run to find the effect of small amounts of antimony on the solid solubility of bismuth in lead. In this set of experiments we encountered the same difficulties met by other workers in this field; the lowering of the conductivity due to solid solution of bismuth in lead is small compared to that of most other substances. The amount of antimony was held constant at 1 per cent. and the bismuth content was varied. The conductivity curves (Fig. 12) obtained from the data in Table 9 show evidence of two breaks. The first possible break occurs with small amounts of bismuth showing the mutual solubility of antimony in lead in the presence of the lead-bismuth solid solution. This is the same as was found in the previous series. The second apparent break comes at 25 per cent. bismuth at 25° C. and at 26 per cent. at 100° C. This agrees fairly well with the values obtained for the solubility of bismuth in pure lead obtained by Herold.²⁵ The existence of the breaks may be proved by a differential method. When the change of conductivity ΔC , divided by the change of composition, Δ per cent., is plotted against per cent. bismuth, the region of the break is clearly shown. From this, therefore, we must conclude that *small* amounts

²⁵ W. Herold: *Loc. cit.*

of antimony have little effect on the total solid solubility of bismuth in lead; the first few per cent. of bismuth is removed by the antimony and then the bismuth acts toward the remainder as if it were pure lead.

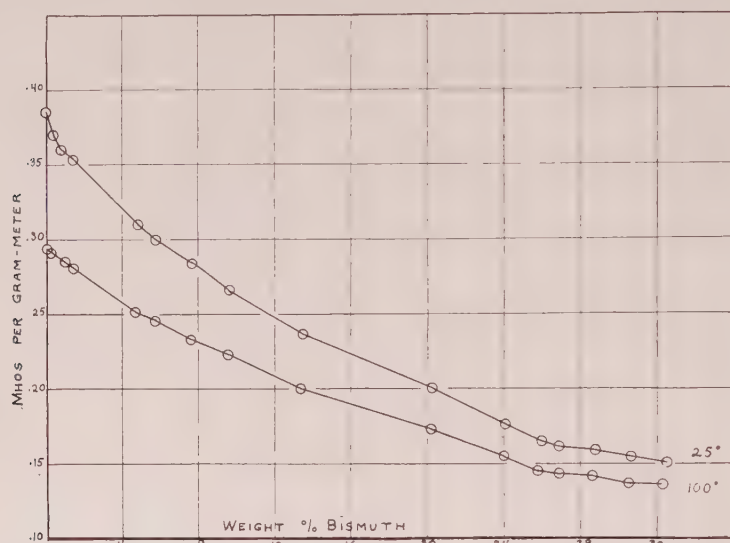


FIG. 12.—CONDUCTIVITY AT 25° AND 100° C. OF 1 PER CENT. ANTIMONY-LEAD-BISMUTH.

TABLE 9.—*Conductivity of the 1 Per Cent. Antimony-lead-bismuth Series in Mhos per Gram-meter*

Per Cent. Bi	Per Cent. Sb	Conductivity, 25° C.	Conductivity, 100° C.
0.0	1.0	0.4060*	0.30805
0.3	1.0	0.38735	0.30626
1.08	0.94	0.37645	0.29864
1.5	1.0	0.36983	0.29431
5.0	1.0	0.32553	0.26369
6.0	1.0	0.31471	0.25658
8.0	1.0	0.29716	0.24420
10.0	1.0	0.27803	0.23181
14.0	1.0	0.24609	0.20929
21.0	1.0	0.20819	0.17964
25.0	1.0	0.18305	0.16065
27.0	1.0	0.17115	0.14847
28.0	1.0	0.16713	0.14865
30.0	1.0	0.16417	0.14503
32.0	1.0	0.15950	0.14036
34.0	1.0	0.15487	0.13954

* Extrapolated value from lead antimony data previously published by Dean and his associates.

In wires containing equal weights of bismuth and antimony, the decrease of the solubility of bismuth in the presence of antimony is brought out (Fig. 13 and Table 10).

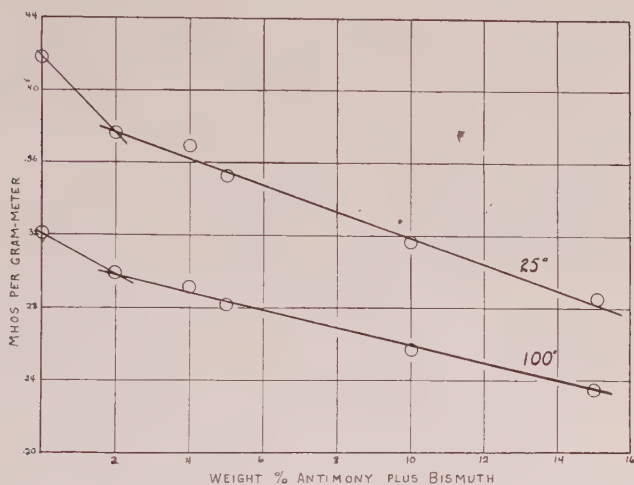


FIG. 13.—CONDUCTIVITY AT 25° AND 100° C. OF WIRES CONTAINING EQUAL WEIGHTS OF ANTIMONY AND BISMUTH.

TABLE 10.—*Conductivity with Equal Weights of Bismuth and Antimony in Mhos per Gram-Meter*

Per Cent. Bi	Per Cent. Sb	Conductivity, 25° C.	Conductivity, 100° C.
0.0	0.0	0.4180	0.3210
1.08	0.94	0.37645	0.29864
2.0	2.0	0.37019	0.29182
2.5	2.5	0.35305	0.28161
5.0	5.0	0.31674	0.25646
7.5	7.5	0.28547	0.23483

There seems to be little difference in the curves obtained at 25° and 100°, but this may be due to the fact that equilibrium was not reached at the lower value. Not enough points were taken to determine the actual position of the break. From these results, however, it is below 1 per cent. The actual solubility is probably closer to 0.5 per cent., as this is the value for the solubility of antimony in lead at 100° C.

The effect of bismuth and antimony on their mutual solid solubility in lead can then be summed up in a few words. Antimony causes a marked decrease in the solid solubility of bismuth in lead when the amount of antimony exceeds the solubility of antimony in lead. Up to

the saturation value of antimony with respect to lead, there is little effect on the solubility of bismuth. The effect of bismuth on the solid solubility of antimony is small. Up to 225° C., one per cent. bismuth has little or no effect on the antimony solubility. The peak of the dispersion hardening curve comes at the same point as in the case of pure lead-antimony alloys. However, the solidus floor of the ternary system slopes down from the lead-antimony line so that by the time 2.0 per cent. bismuth is added, wires containing 2.5 per cent. antimony partially melt at 225° C.

SUMMARY

The system lead-antimony-bismuth has been studied and the following points brought out:

1. The liquidus surface has been obtained and a ternary diagram drawn.
2. A series of ternary solid solutions rich in antimony and bismuth has been demonstrated.
3. The solid solutions in the lead corner have been studied.
4. Small amounts of antimony have little effect on the solid solubility of bismuth, but larger amounts remove bismuth from solid solution.
5. Bismuth has little effect on the solid solubility of antimony up to 225° C.
6. Small amounts of bismuth have little effect on the dispersion hardening of lead-antimony alloys. Larger amounts decrease, materially, the hardening of these alloys, due to the lowering of the temperature range over which heat treatment is possible.

The Lead Corner of the Lead-antimony-tin System

BY RALPH A. MORGEN AND EVELYN H. ROBERTS

The system lead-antimony-tin has been rather extensively investigated as far as the liquidus and solidus surfaces are concerned. From the work of Campbell and Elder²⁶ and of Loebe,²⁷ the ternary diagram pictured in Fig. 14 was obtained. The present investigation was undertaken in order to ascertain what happens in the solid phases below the solidus surface in the region where lead is the predominating constituent. The change of solid solubility with temperature is important in that it determines the dispersion hardening properties of the mixtures.

²⁶ W. Campbell and F. C. Elder: Notes on Lead-tin-antimony. *Jnl. Soc. Chem. Ind.* (1911) **30**, 693.

²⁷ R. Loebe: Über die Konstitution der ternären Legierungen von Blei, Zinn und Antimon. *Metallurgie* (1911) **8**, 7.

EXPERIMENTAL RESULTS

The experimental procedure was the same as that used in the lead-antimony-bismuth system in the previous section. In addition, however, some conductivity values on "worked" wires were obtained. The "worked" samples were made by running the wires through the rolls into the form of tape whose thickness was about one-third the original

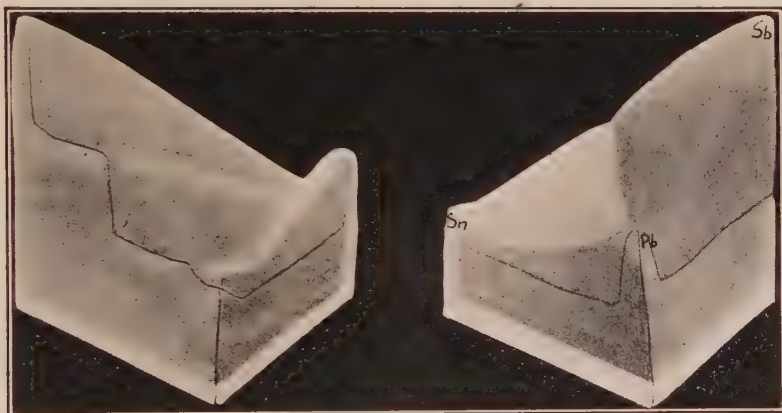


FIG. 14.—PLASTER MODEL OF SYSTEM LEAD-ANTIMONY-TIN (CAMPBELL AND ELDER AND LOEBE).

diameter of the wire. The results may be divided into six sets of experiments:

1. The solubility of antimony²⁸ in lead.
2. The solubility of tin in lead.
3. The solubility of tin in lead in presence of 0.5 per cent. antimony.
4. The solubility of tin in lead in presence of 2.0 per cent. antimony.
5. The solubility of antimony in lead in presence of 0.5 per cent. tin.
6. The solubility of antimony and tin along the 45° line containing equal weight per cents. (and also mol per cents.) of tin and antimony.

2. The solubility of tin in lead had been investigated by Parravano.²⁹ In order to be sure that our method on wires was comparable with the previous work, which was done by the method of Bucher,³⁰ several comparison runs were made. These results, together with those of Parravano's are given in Table 11 and plotted in Fig. 15. This solid-solution range has also been found by Guillet³¹ by a hardening method. He finds

²⁸ R. S. Dean, L. Zickrick and F. C. Nix: *Loc. cit.*

²⁹ Parravano: *Gass. chim. ital.* (1920) **50**, **I**, 83.

³⁰ A. Bucher: Untersuchungen über die Konstitution der Zinn-Kadmium und der Zinn-Wismut-Legierungen. *Zeitschr. anorg. allgem. chemie.* (1916) **98**, **I**, 97.

³¹ L. Guillet: Les Phénomènes de Trempe et leur Généralisation. *Chim. et Ind.* (1922) **7**, 211.

TABLE 11.—*Solid Solubility of Tin in Lead*

Per Cent. Tin	Degrees Centigrade	Source
1.5	25	Parravano
3.0	50	Parravano
5.0	75	Parravano
6.5	100	Parravano
10.0	150	Parravano
12.5	162	Parravano
13.5	170	Parravano
14.5	175	Parravano
1.7*	28	Morgen and Roberts
2.4	28	Morgen and Roberts
5.8	100	Morgen and Roberts
9.5	150	Morgen and Roberts

* Worked samples.

considerable change in solubility between 150° and 180° C. These results check the hardening data given later.

3. The introduction of small amounts of antimony to the tin-lead mixtures has little apparent initial effect on the solubility of the tin.

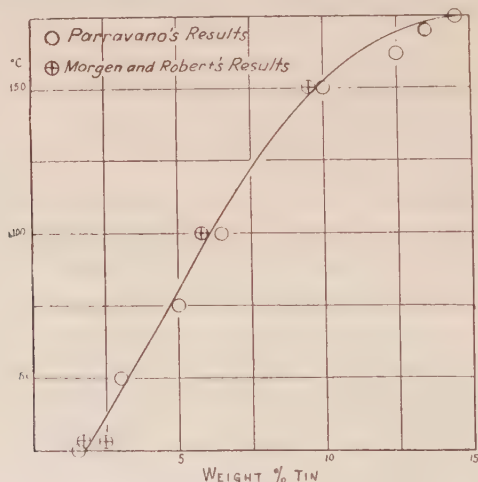


FIG. 15.—COMPARISON OF AUTHORS' VALUES FOR SOLUBILITY OF TIN IN LEAD COMPARED WITH THOSE OF PARRAVANO.

This effect is demonstrated in Fig. 16, the values for which were obtained from Table 12. From these results it can be seen that at 67° C. there is a possible break in the curve in the vicinity of 4 per cent. tin; the second break at 8.0 per cent. tin is due to the past history of the wire (temperature of extrusion). This break tends to disappear on working the wires.

At 150° C. there is a break at 10 per cent. tin. While the points do not all fall on the line at the lower temperature, it did not appear advisable to continue the experiments long enough to permit all the wires to reach

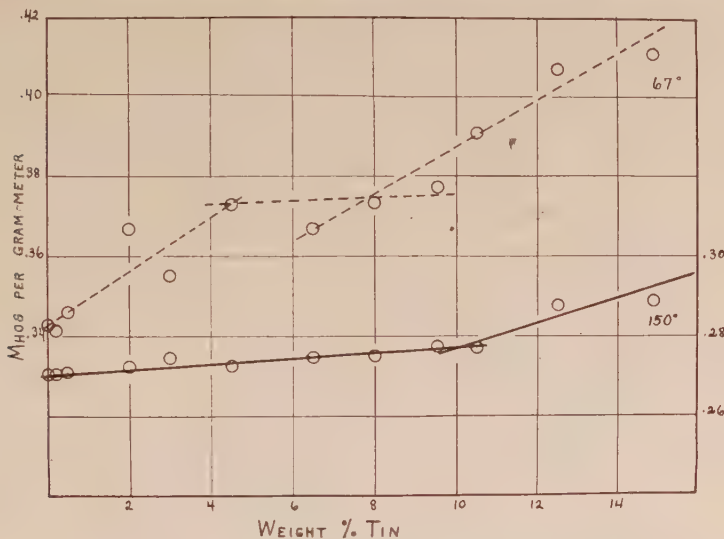


FIG. 16.—CONDUCTIVITY AT 67° AND 150° C. OF 0.5 PER CENT. ANTIMONY-LEAD-TIN.

The 67° curve is dotted to indicate the source of possible breaks; insufficient data were obtained to give exact location.

equilibrium. Enough of the wires were cold worked, to speed up the equilibrium process, to demonstrate that the lines as drawn are essentially correct.

TABLE 12.—Conductivity in Mhos per Gram-meter at 67° and 150° Centigrade for the 0.5 Per Cent. Sb-Pb-Sn Series

Per Cent. Sn	67° C.	150° C.
0.0	0.343*	0.270*
0.2	0.34165	0.27091
0.5	0.34596 (0.34607)	0.26960 (0.27110)
1.0	0.33868	
2.0	0.36732	0.27262
3.0	0.35512	0.27462
4.5	0.37329	0.27269
6.5	0.36736	0.27482
8.0	0.37352	0.27500
9.4	0.37754	0.27756
10.5	0.39148	0.27736
12.5	0.40670	0.28789
14.7	0.41099	0.28873

* Interpolated values from other data.

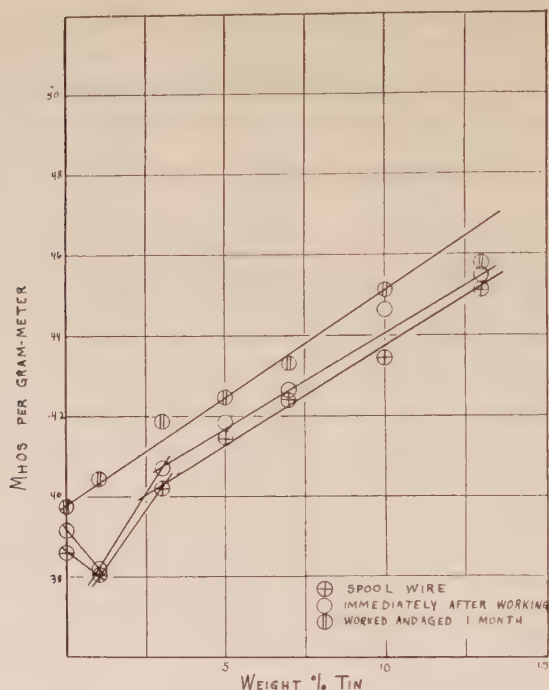


FIG. 17.—CONDUCTIVITY AT 28° C. OF 2 PER CENT. ANTIMONY-LEAD-TIN (WORKED).

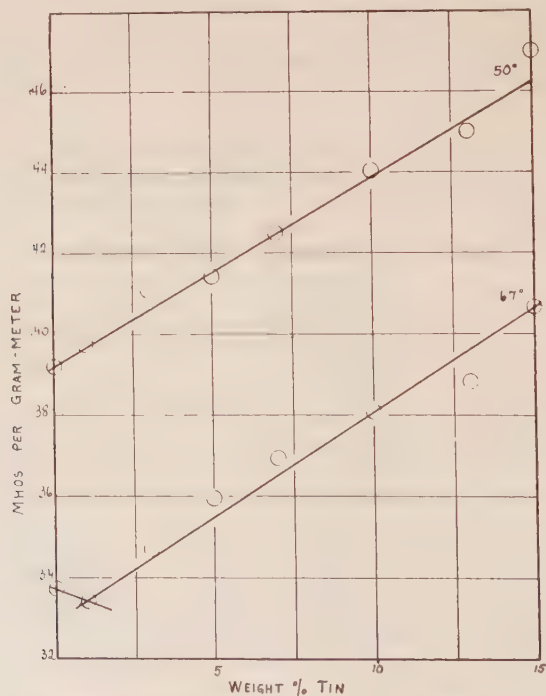


FIG. 18.—CONDUCTIVITY AT 50° AND 67° C. OF 2 PER CENT. ANTIMONY-LEAD-TIN. Compare with Fig. 17 to show effect of "cold work."

4. As the amount of antimony is increased to 2 per cent., the solubility of tin falls off rapidly. The effect of cold working in order to obtain equilibrium at the lower temperatures is effectively demonstrated in Fig. 17. The spool wire had been in the laboratory for several months before being tested. The break at 1.00 per cent. tin was evidently due to its past history and consequent inability to reach equilibrium. After equilibrium is reached there is no break in the solubility curve at either 28° (Fig. 18) or 50°. The 50° values were held at 50° for several days, then quenched and measured at room temperatures. At 67° there seems

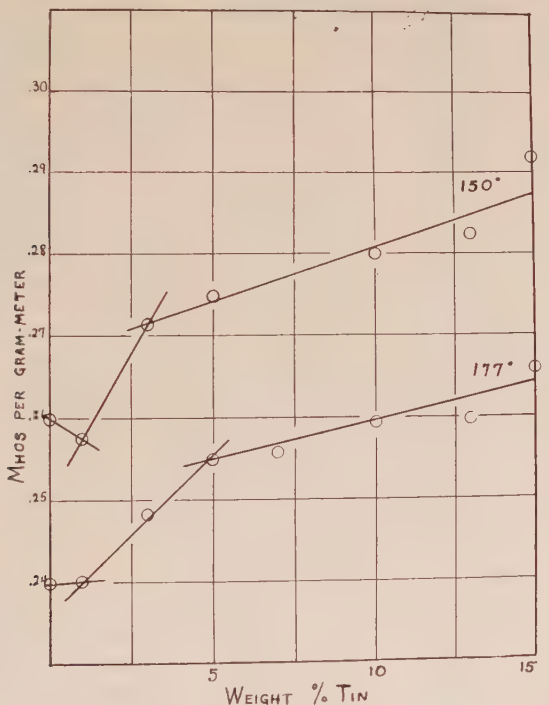


FIG. 19.—CONDUCTIVITY AT 150° AND 177° C. OF 2 PER CENT. ANTIMONY-LEAD-TIN SERIES.

to be an appreciable solubility of tin, but less than 1 per cent. It probably is a very small amount and might disappear on continued working. At 150° there are two breaks (Fig. 19) at 1 per cent. and 3 per cent., while at 177° the two breaks come at 1 per cent. and 4.5 per cent. tin. The results for the 2 per cent. antimony line are summarized in Table 13.

5. The effect of small amounts of tin on the solubility of antimony in lead is rather pronounced at low temperatures. At room temperature (Fig. 20) the solubility of antimony remains 0.7 per cent. in the presence of 0.5 per cent. tin, even after working, so this is evidently a fair value. At 67° (Fig. 21) the solubility is 1 per cent.; at 150°, 1.3 per

cent., and at 207°, 2.0 per cent. All the experimental values for the 0.5 per cent. tin line are given in Table 14.

TABLE 13.—*Conductivity Data in Mhos per Gram-meter for the 2 Per Cent. Sb-Pb-Sn Series*

Per Cent. Sn	Per Cent. Sb	28° Centigrade			67° C.	150° C.	177° C.
		Spool Wire	1 Hour after Working	Worked and Aged 1 Month			
0	2	0.3861	0.3918	0.3978	0.33746	0.25994	0.24001
1	2	0.3804	0.3823	0.4030	0.33631	0.25595 0.25920	0.24034
3	2	0.4020	0.4070	0.4190	0.34721	0.27450 0.26830	0.24838
5	2	0.4151	0.4188	0.4248	0.35953	0.27525 0.27267	0.25531
7	2	0.4240	0.4265	0.4335	0.36950	0.28162 0.28050	0.25598
10	2	0.4348	0.4465	0.4512	0.38108	0.27870 0.28157	0.25977
13	2	0.4515	0.4550	0.4580	0.38851	0.28237	0.25993
15	2	0.4730	0.4774	0.4985	0.40670	0.29212	0.26599

TABLE 14.—*Conductivity in Mhos per Gram-meter for the 0.5 Per Cent. Sn-Sb-Pb Series*

Per Cent. Sb	Per Cent. Sn	28° Centigrade			67° C.	150° C.	177° C.
		Spool Wire	1 Hour after Working	Worked and Aged 1 Month			
0.0	0.5	0.4125	0.4148	0.4177	0.35510	0.28026	0.23856
0.5	0.5	0.3942	0.3958	0.4090	0.34596	0.26960	0.23139
0.7	0.5	0.3915	0.3920	0.4048	0.33947	0.26681	0.23164
1.0	0.5	0.3860	0.3880	0.4068	0.33417	0.26472	0.22674
1.3	0.5	0.3835	0.3858	0.4025	0.33420	0.26322	0.22213
1.7	0.5	0.3823	0.3837	0.4035	0.33261	0.26144 0.25955	0.21928
2.0	0.5	0.3772	0.3796	0.4010	0.33586	0.26150 0.25962	0.21795
2.5	0.5	0.3797	0.3825	0.4013	0.32967	0.25641	0.21687
3.0	0.5				0.32740	0.25477 0.25978	0.21568
3.5	0.5				0.33100	0.26020 0.25831	
4.0	0.5				0.32672	0.25721 0.25959	0.21495
5.0	0.5				0.32112	0.25573	0.21537
6.0	0.5				0.32750	0.25501	0.20155

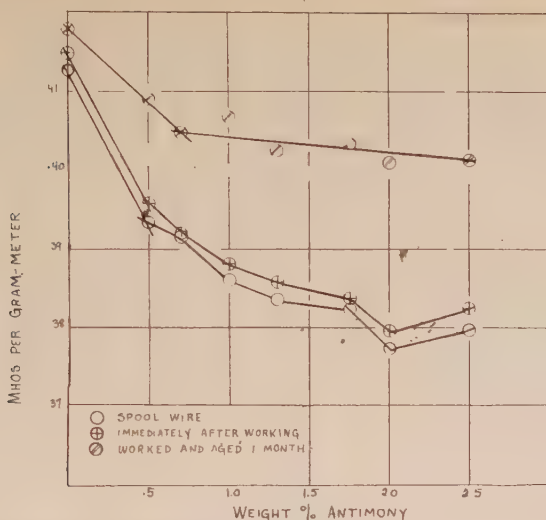


FIG. 20.—CONDUCTIVITY AT 28° C. OF 0.5 PER CENT. TIN-LEAD-ANTIMONY (WORKED).

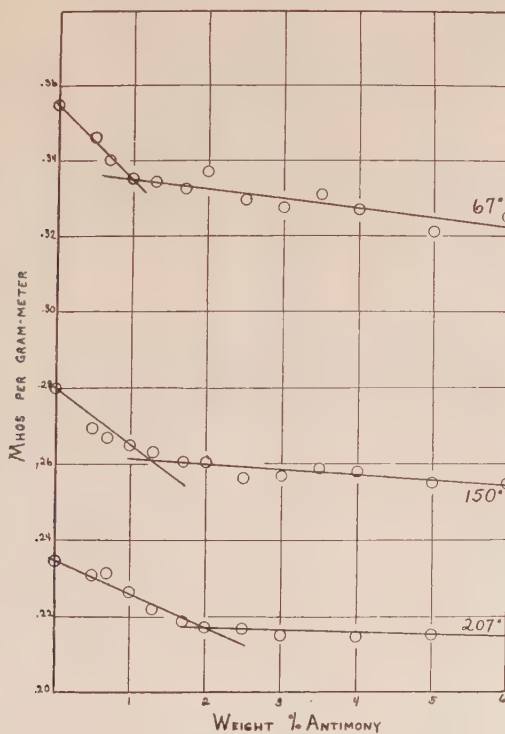


FIG. 21.—CONDUCTIVITY AT 67°, 150°, AND 207° C. OF 0.5 PER CENT. TIN-LEAD-ANTIMONY SERIES.

Compare with Fig. 20 to show effect of "cold work."

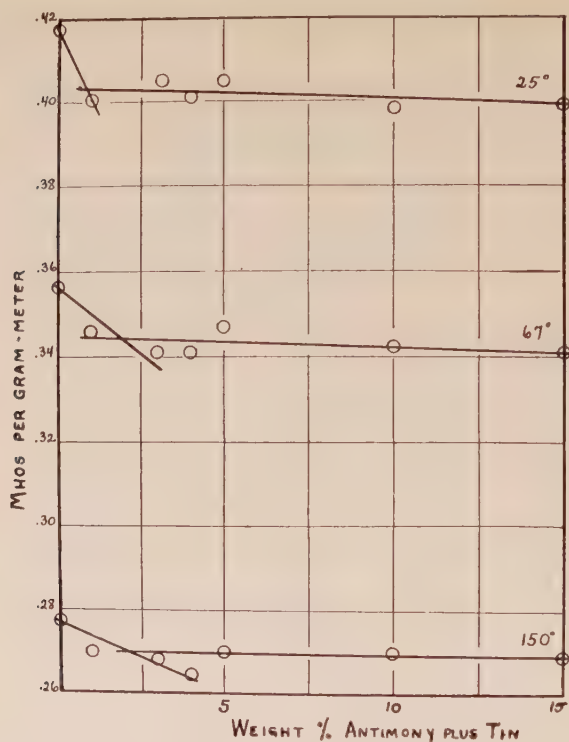


FIG. 22.—CONDUCTIVITY AT 25°, 67° AND 150° C. OF EQUIMOLAR AMOUNTS OF ANTIMONY AND TIN.

TABLE 15.—Conductivity in Mhos per Gram-meter for Wires Containing Equimolar Amounts of Antimony and Tin

Per Cent. Sb	Per Cent. Sn	25° C.	67° C.	150° C.
0.0	0.0	0.4180	0.3568	0.2775
0.5	0.5	0.4005	0.34607	0.26960
			0.34596	0.27110
1.5	1.5	0.4055	0.34130	0.26827
				0.26840
2.0	2.0	0.4010*	0.3412*	0.2645*
2.5	2.5	0.4050	0.34645	0.26672
			0.34730	0.27244
5.0	5.0	0.3985	0.34230	0.26628
				0.27344
7.5	7.5	0.3990	0.34161	0.26891

* Interpolated from other data

6. On the 45° line, containing equivalent amounts of tin and antimony, there remains appreciable solubility even at room temperature. At 25° C. the solubility is about 0.4 per cent. of both tin and antimony (Fig. 22), while at 67° there is about 0.8 per cent. of each. From 67° to 150° the change in solubility is only 1.00 per cent. of each. The values obtained along this line are given in Table 15.

DISCUSSION

From these data it is possible to construct the isotherms for the solid solubility of antimony and tin in lead at three different temperatures—room temperature, 67° , and 150° C. (Fig. 23). The use of such isotherms should determine the “age hardening” or “dispersion hardening”

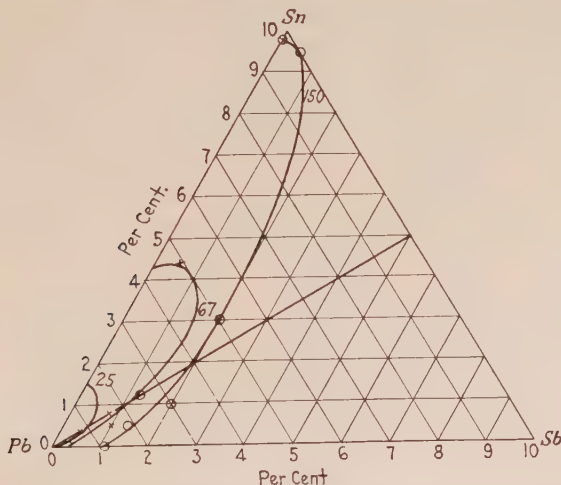


FIG. 23.—LEAD CORNER OF SYSTEM LEAD-ANTIMONY-TIN SHOWING SOLID SOLUBILITY ISOTHERMS.

properties of these alloys. The effect of small amounts of tin on the solubility of antimony is marked at the lower temperatures. The tin has a tendency to hold the antimony in solution below 67° , but has little effect on the solubility of antimony at 150° or above. The result is that small amounts of tin in an antimony-lead alloy are deleterious from a dispersion hardening standpoint. Small amounts of antimony seem to have little effect on the solubility of tin, but as more antimony is added, the solubility falls off rapidly. The temperature effect is small near the lead-tin axis, being practically the same as if no antimony were present. However, in the region of the equimolar line, the isotherms approach very closely together, so that alloys in this region would show very little hardening effect. The best hardeners in this system would be alloys high in tin with small amounts of antimony. The absolute increase in hardness would be small, due to the fact that the separating constituent still

has an appreciable solubility, permitting more rapid diffusion through the soft lead lattice and growth of the larger tin particles at the expense of the smaller. Agglomeration would then take place. High-tin alloys, therefore, would overage readily and become soft. This is exemplified in Table 16. The alloys containing 0.5 per cent. tin and varying amounts of antimony show more hardening than those above. However, the increase in hardness is less than that in the absence of tin. This is illustrated in Table 17. When 0.5 per cent. tin was present, the heat treatment was performed at 207° C. rather than 225° C., due to the lowering of the solidus floor. Alloys containing this amount of tin show decided evidence of breaking down after prolonged heat treatment at 225° C. Many samples will stick together, which shows evidence of liquid formation.

TABLE 16.—*Tensile-strength Tests in Kilograms per Square Millimeter on Alloys Containing 0.5 Per Cent. Antimony and Varying Amounts of Tin after Heat Treatment*

Composition		Quench. Temp., Degrees Cent.	Tensile Strength after Aging at Room Temperature			
Per Cent. Sn	Per Cent. Sb		1 Hour	4 Days	10 Days	13 Days
0.5	0.5	150	2.20	2.39	2.42	2.39
3.0	0.5	150	3.24	3.24	3.24	3.12
4.5	0.5	150	3.47	3.51	3.36	3.22
6.5	0.5	150	3.59	3.55	3.43	3.42
8.0	0.5	150	3.63	3.51	3.67	3.46
9.4	0.5	150	4.06	4.11	3.67	3.59
10.5	0.5	150	4.15	4.02	3.83	3.48
12.5	0.5	150	4.46	3.99	3.79	3.64
14.7	0.5	150	4.11	3.95	3.71	3.67

TABLE 17.—*Tensile Strength in Kilograms per Square Millimeter of Alloys Containing 0.5 Per Cent. Tin and Varying Amounts of Antimony after Heat Treatment*

Composition		Quench. Temp., Degrees Cent.	Time of Age at Room Temperature			
Per Cent. Sn	Per Cent. Sb		1 Hour	4 Days	10 Days	13 Days
0.5	0.0	207	1.67	1.79	1.88	1.88
0.5	0.5	207	2.30	2.33	2.48	
0.5	0.7	207	2.45	2.58	2.74	2.73
0.5	1.0	207	2.58	2.86	3.86	3.87
0.5	1.3	207	2.57	3.12	3.55	3.58
0.5	1.7	207	3.05	3.87	4.37	4.19
0.5	2.0	207	3.10	4.16	4.51	4.46
0.5	2.5	207	3.22	4.29	4.44	4.36
	2.5	235	3.20	7.00	6.70	

The effect of the large increase of solubility of tin between 150° and 180° C., demonstrated by Guillet,³² is brought out in a series of hardening experiments performed by C. R. Hayward.³³ His results are reproduced in Table 18. In this case the large increase came between 185° and 200° because the solidus floor of the ternary system slopes up from 180°, the ternary eutectic, toward 235°, the lead-antimony eutectic. The

TABLE 18.—*Brinell Hardness on Alloy Containing 3 Per Cent. Antimony, 3 Per Cent. Tin, 94 Per Cent. Lead**

Temp. to which Heated, Degrees Cent.	Before Heating	Time of Aging after Heating				
		1 Hour	2 Days	4 Days	5 Days	6 Days
146	15.3	14.5	14.0	14.8	15.3	14.2
155	15.3	13.7	11.9	13.0	13.5	14.2
170	15.3	12.8	12.8	12.8	13.7	13.7
185	14.8	12.4	12.4	12.8	13.3	14.0
200	14.8	12.4	13.3	13.3	15.9	16.5
218	14.8	12.8	17.0	19.3	19.3	19.3
235	14.5	13.3	21.0	21.8	23.3	23.8

* Hayward's values.

sample that was heated to 235° may have contained some molten ternary eutectic, but this would tend to increase the speed of dispersion hardening, provided the alloy was not roughly handled at the higher temperatures. We have several cases of alloys of this system being heated above the lead-antimony eutectic, as high as 265° C., which hardened very rapidly after quenching. Evidently the little globules of molten eutectic remain dispersed and act as hardness centers, giving a very fine dispersion.

TABLE 19.—*Brinell Hardness on Lead-antimony-tin Alloys Heated to 260° C. and Aged at Room Temperature*

Composition		Hardness after Aging		
Per Cent. Sb	Per Cent. Sn	0 Days	1 Day	4 Days
4.0	0.5	15.0	19.0	22.0
2.5	0.5	13.0	24.0	27.0
2.0	0.5	11.7	22.0	26.0

³² L. Guillet: *Loc. cit.*

³³ R. S. Dean, L. Zickrick and F. C. Nix: *Op. cit.*, 536 (see discussion by C. R. Hayward).

CONCLUSIONS

1. The mutual solid solubility of tin and antimony in lead has been determined.
2. Small amounts of tin have little effect on the solid solubility of antimony at elevated temperatures, but tend to hold the antimony in solution at lower temperatures.
3. Small amounts of antimony have little effect on the solid solubility of tin.
4. Larger amounts of antimony decrease the solubility of tin rapidly.
5. Ternary lead-antimony-tin alloys show less dispersion hardening than binary lead-antimony alloys.
6. Tin is deleterious to the dispersion hardening of lead-antimony alloys.
7. At temperatures close to the solidus surface, there is a large increase in the solubility of tin.
8. The presence of tin in lead-antimony alloys appreciably lowers the temperature at which heat treatment may be performed.

ACKNOWLEDGMENT

This work has of necessity been spread over a period of several years, and has been carried on by several investigators. We wish to thank Dr. A. W. Coffman for some of the values, and E. F. Salchow for work done on the photomicrographs. The entire investigation has been performed under the direction of R. S. Dean.

DISCUSSION

W. CAMPBELL, New York, N. Y. (written discussion).—This paper is a decided contribution to our knowledge of the lead-antimony alloys and the authors are to be congratulated on their painstaking work. The ternary diagram Pb-Sb-Cu is of special interest. In the spring of 1917 Richard P. E. Hermsdorf³⁴ investigated this series, because the cost of tin was then exceptionally high and there was a demand for a substitute in bearing metals. Lead-base alloys containing antimony and copper had been tried in the past but with varying results. It therefore seemed worth while to examine the ternary system especially as regards the two-liquid area. Mr. Hermsdorf's determinations are summarized in Fig. 24. The work was continued in 1920 especially around the lead corner and the point *F* more accurately determined at 96 per cent. lead. As regards the constitution of the alloys solidifying in the single-liquid field, the question is complicated by the fact that the Cu-Sb diagrams are not in agreement. Reimann's diagram of 1920 is given here (Fig. 25). It differs from that of Carpenter (1913) chiefly in the location of the maximum *J* and the occurrence of a eutectoid transformation *PN* at 430° C. There is also a lack of agreement as to the exact location of the points *J'* and *K'* in the copper-lead system. These differences are shown in Table 20.

³⁴ Thesis. Degree of Met. E., Columbia University.

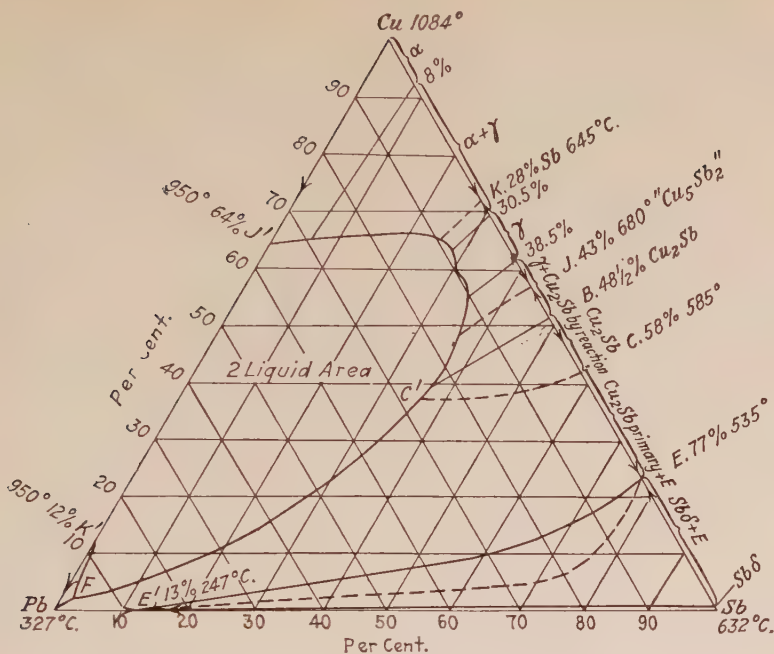


FIG. 24.—PB-SB-CU PROVISIONAL DIAGRAM, 1918-20.

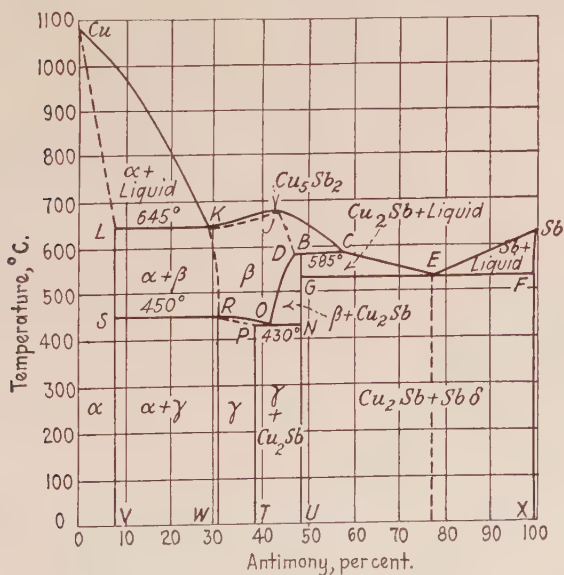


FIG. 25.—REIMANN'S DIAGRAM OF 1920.

TABLE 20.—*Location of Points in Pb-Sb-Cu System*

Copper-Antimony								
Point	Guertler		Carpenter			Reimann		
	Per Cent. Sb	Degrees Cent.	Per Cent. Sb	Per Cent. Cu	Degrees Cent.	Per Cent. Sb	Per Cent. Cu	Degrees Cent.
K.....	31	628	28		646	28		645
J.....	38	682	38		680	43		680
C.....	59	587	59		585	57		585
E.....	77	525	78		530	76.5		535
Cu α			8			8		
Sb δ				0.5			0.5	
γ			30-38.5			30.5-38.5		

Copper-Lead								
Point	Roberts-Austen		Guertler		Friedrich and Leroux		Friedrich and Wachlert	
	Per Cent. Cu	Degrees Cent.	Per Cent. Cu	Degrees Cent.	Per Cent. Cu	Degrees Cent.	Per Cent. Cu	Degrees Cent.
J'.....	62-63		63		64		54	
K'.....	23	950	16	950	12	950	19	953

The lead-rich matrix freezes at 326° C.

All the authorities agree as to the occurrence of Cu₃Sb, but not in regard to the maximum *J*. Guertler designates this as Cu₃Sb, and so does Carpenter. Reimann finds it to be Cu₁₅Sb₂, Kurnakoff and Beloglasoff³⁵ point out that *J* occurs at 72 atomic per cent. of copper. Furthermore, the curves for electric conductivity and for thermal coefficients do not show any singular point in this region and therefore neither Cu₃Sb₂ nor Cu₃Sb exists.

In our work, which was based on microstructure alone, we found that in the area K' F Pb there occurred crystals of Cu α or Cu₂Sb, depending on the amount of antimony present, in a lead-rich matrix. The binary line EE' appeared to end very close to the lead-antimony eutectic. From microstructure alone it might be drawn much lower as shown by the dotted line, because of the difficulty in determining when Sb and when Cu₂Sb is the first constituent to crystallize out, but the thermal determinations of Schack and the present authors show that the upper line is nearer the true one.

The main difference between our results and those of the present authors is in the location of the reaction line *PT* in their diagram. Schack gives this as a smooth curve ending at the lead corner. Our determination *CC'* from microstructure was based on the supposed primary crystallization of Cu₁₂Sb. We noticed two distinct types; namely, grains and rosettes on the one hand and plates and needles on the other, and

³⁵ *Rev. de Mét. Extraits*. (1922) **19**, 588.

Jnl. Russian Physico-Chemical Soc. (1916) **48**, 700.

had we taken the former to indicate a peritectic reaction, our line would have been in substantial agreement with that of the present authors.

In fairness to Mr. Hermsdorf, it should be stated that his results were not published because it was hoped that they could be made more complete by analyzing the two layers of alloys in the two-liquid area and thus adding tie-lines to the diagram. But time for this, like the Greek Kalends, never came.

G. O. HIERS, Brooklyn, N. Y. (written discussion).—This paper covers in a comprehensive fashion three ternary systems. Those who have studied only binary equilibrium diagrams can begin to appreciate the thought, painstaking work, and time involved in the preparation of this paper.

Therefore it is with some misgivings that attention is called to a very small portion of the work. On page 322 it is stated that the addition of up to 2 per cent. Cu to the Pb-Sb binary eutectic mixture was not detected in the cooling curves. The users of lead alloys are very much concerned with this portion of the diagram, so we have investigated the matter a little further. It is difficult, or perhaps impossible, to detect the degree of solubility of such small amounts of copper in this alloy by ordinary or refined cooling-curve methods, therefore the problem was attacked in a different way. We tried to find how much copper we could dissolve in the alloy made up of 13 per cent. Sb and 87 per cent. Pb. Equilibrium was attained at 300° C., showing a solubility of 0.13 per cent. Cu in the alloy while at 400° C. we tentatively place the solubility at 0.5 per cent. Cu.

R. S. DEAN, Chicago, Ill.—This work of Professor Campbell not only antedates our work but also the diagram of Schack on which our work was to a considerable extent based. In regard to the two points raised by Professor Campbell—namely, the position of that ternary eutectic which is the same one discussed by Mr. Hiers—I believe Morgen says that point is at less than 2 per cent. We do not know how much less than 2 per cent; as near as we could tell from our cooling, it was practically identical with the lead-antimony eutectic.

A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders

BY CARL E. SWARTZ,* SELBY, CALIF.

(New York Meeting, February, 1928)

ALTHOUGH a number of articles appeared during the war advocating the use of cadmium in lead-tin solders, very little information of value can be found in the literature regarding the properties of solders containing cadmium. In most of the published articles the cadmium seems to have been considered merely as a partial substitute for tin in a tin-lead alloy rather than as an essential constituent of a ternary alloy. The primary object of the substitution of cadmium for tin was to lessen the amount of tin required, at a time when the latter was scarce and high-priced, and thus to produce a cheaper solder. While this object was accomplished, the new properties resulting from a change from a binary lead-tin alloy to a ternary lead-tin-cadmium alloy were not given proper consideration in many cases.

For the past few years, the American Smelting & Refining Co. has been marketing a very considerable amount of cadmium in the form of lead-tin-cadmium alloys for use as solders for certain special purposes, and the successful use of these solders suggested that if more extensive knowledge were available concerning the properties of lead-tin-cadmium alloys of various compositions their field of usefulness might be materially extended.

The investigation described in the present paper was undertaken to obtain this information and, by means of tests under conditions approaching those of practical use, to determine the suitability of cadmium solders for various purposes.

CHARACTERISTICS AND REQUIREMENTS OF SOLDERS IN GENERAL

General Physical Properties.—When cast into bars, solder should present a smooth and bright appearance free from oxide inclusions and bubbles. Ductility should be as great as possible without sacrificing tensile strength, and vice versa. Hardness and specific gravity are not of any great importance.

Melting Characteristics.—The melting or solidification range is important. This statement applies both to the extent of the range and to the actual temperature at which complete solidification occurs. A rather narrow solidification range is desirable in soft solders in order that solidification may take place quickly. The solder should have high fluidity at temperatures only slightly above its melting range. For a

* Research Department, American Smelting & Refining Co.

wiping solder, on the other hand, a wide solidification range is necessary, in order that the solder may remain in a pasty condition while the joint is being made; the solidification range should lie at temperatures low enough so that the wiping cloth will not burn during the operation. Solders having a high melting point are valuable for use in soldering equipment that is to be used at elevated temperatures.

Soldering Characteristics.—Any alloy or metal that will readily alloy with other metals or alloys at ordinary soldering temperatures may be considered as a solder. In order to have commercial value for the purpose, it must be capable of readily forming joints of high tensile and shear strength together with high ductility. The production of such joints depends not only on the strength and ductility of the solder itself, but is also largely dependent on the ease with which it alloys with or “wets” the metals to be joined. The latter is especially important in machine soldering operations where soldering is carried on with extreme rapidity and capillary action is depended upon very largely to draw the solder into the joint.

The property of “wetting” or flowing on the work is greatly affected by temperature and by the soldering fluxes used, and different solder alloys may require different temperatures and fluxes to give best results.

In general, the thinner the layer of solder between the metals joined, the greater will be the strength of the joint, so long as the film of solder is continuous.

PREPARATION OF ALLOYS FOR EXPERIMENTAL INVESTIGATION

All of the alloys studied were prepared in the following manner: The required amount of each constituent pure metal was weighed out to an accuracy of 0.25 per cent. or better. The metal of lowest melting point was placed in a graphite crucible, covered with high flash-point oil, and melted in an electrically heated pot furnace. The remaining metal or metals were then added piece by piece with occasional stirring until the whole was molten. The oil prevented any oxidation, with resultant change in composition. After several minutes stirring, the alloy was allowed to cool to complete solidification, during which a time-temperature cooling curve was plotted to obtain the solidification range.

Temperatures were taken with a nitrogen-filled mercury thermometer with the bulb immersed directly in the metal. This thermometer was checked frequently against a standard thermometer. No particular effort was made to attain extreme accuracy in the temperature measurements, but they are believed to be accurate to within $\pm 5^\circ \text{C}$.

The solidification ranges of all alloys of the lead-tin-cadmium system studied were found to agree closely with the freezing-point diagram of Stoffel.¹ On the diagram as given by Stoffel the alloy compositions are

¹ A. Stoffel: Untersuchungen über binäre und ternäre Legierungen von Zinn, Blei, Wismut und Cadmium. *Zeitschr. f. anorg. Chem.* (1907) **53**, 137.

expressed in atomic per cents. We have converted these to percentages by weight and the freezing-point diagram based on Stoffel's data, with compositions expressed in weight percentages, is given in Fig. 1.

The compositions of the alloys in this system, which were studied during the course of the present investigation, are shown on the diagram, designated by the letters by which they will be referred to in the following pages.

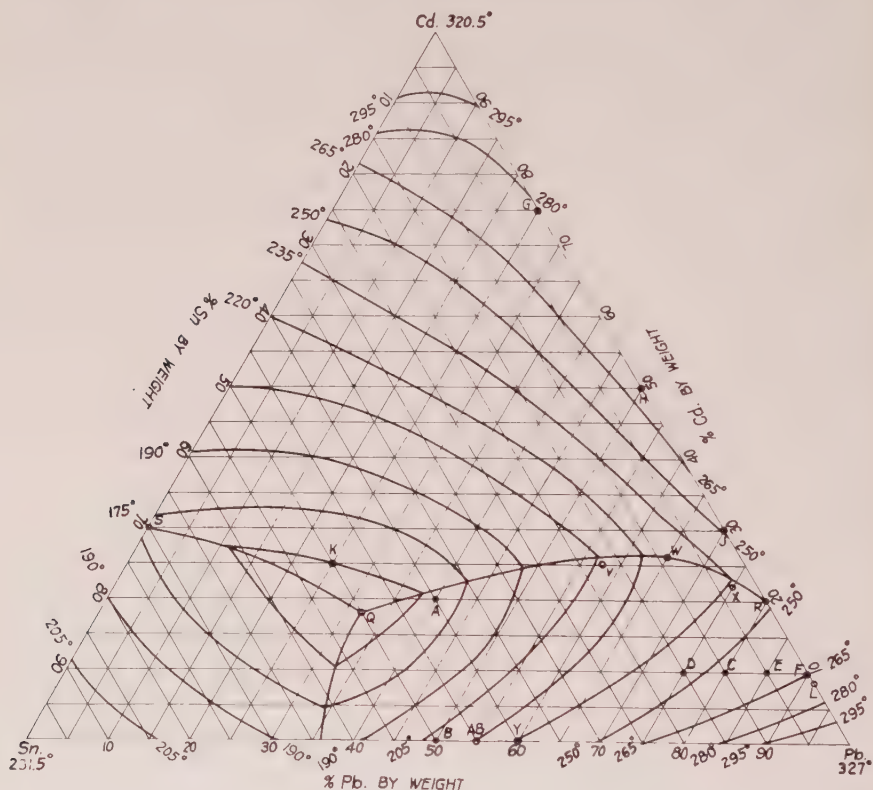


FIG. 1.—FREEZING-POINT DIAGRAM OF LEAD-TIN-CADMIUM ALLOYS.

Reasons for Choice of Alloys

The choice of the particular alloys to be studied in this investigation was influenced by several factors. Some were chosen as representing certain critical points on the freezing-point diagram, such as binary and ternary eutectics; others were selected more or less at random, as representative of certain areas on the diagram; while still others were chosen in an endeavor to meet as nearly as possible specifications as to solidification range and lead content which were set by certain consumers who were interested in the use of cadmium solders for specific purposes.

It will be noted that most of the ternary alloys studied lie in the lead corner of the diagram. The reason for this is that a comparatively high

proportion of lead is required to bring the cost of the alloy low enough to compete with lead-tin solders, for most purposes. Alloys containing very high proportions of cadmium were not studied because of the increased tendency to oxidation when a large percentage of cadmium is present.

Solidification Ranges

The solidification ranges of the alloys studied, as taken from our cooling curves, are given in Table 1. To serve as standards of comparison

TABLE 1.—*Solidification Ranges*

Code Letter	Composition, Per Cent.			Solidification Range			
	Pb	Sn	Cd	Total Range, °C.	Primary Range, °C.	Secondary Range, °C.	Final Eutectic Temp., °C.
B	50	50		210–181	210–181 ^a		181
Y	60	40		240–181	240–181 ^a		181
AB	54	46		222–181	222–181 ^a		181
F	90		10	274–249	274–249 ^f		249
G	25		75	281–249	281–249 ^g		249
H	50		50	274–249	274–249 ^g		249
J	70		30	264–249	264–249 ^g		249
L	91.5		8.5	276–249	276–249 ^f		249
R ^a	80		20				249
S ^b		70	30				176
A	40	40	20	165–145	165–155 ^h	155–145 ^k	145
C	80	10	10	253–145	253–193 ^h	193–145 ^k	145
D	75	15	10	245–145	245–175 ^h	173–145 ^k	145
E	85	5	10	260–145	260–218 ^h	218–145 ^k	145
K	25	50	25	160–145	160–148 ⁱ	148–145 ^m	145
Q ^c	32	50	18				145
V	58	17	25	208–145	208–204 ^h	204–145 ^k	145
W ^d	65	9	26	222–145		222–145 ^k	145
X	75	3	22	237–145	237–235 ^h	235–145 ^k	145

^a Lead-cadmium eutectic.

^b Tin-cadmium eutectic.

^c Lead-tin-cadmium eutectic.

^d Alloy lies on the lead-cadmium binary eutectic line, consequently has no primary solidification range.

^e Primary crystals consist of lead containing some tin in solid solution.

^f Primary crystals consist of lead containing some cadmium in solid solution.

^g Primary crystals consist of cadmium containing some lead in solid solution.

^h Primary crystals consist of lead containing some cadmium and tin in solid solution.

ⁱ Primary crystals consist of cadmium containing some lead and tin in solid solution.

^k Secondary crystals are the binary eutectic of cadmium and lead.

^m Secondary crystals are the binary eutectic of tin and cadmium.

son, three lead-tin alloys are given in the table, followed by the lead-cadmium alloys, the tin-cadmium eutectic alloy, and the lead-tin-cadmium alloys.

Lead-tin-cadmium-bismuth Alloys

In an effort to fill a demand for solders of very low melting point, some alloys were made up containing bismuth as well as lead, tin, and cadmium. It was found that the presence of large amounts of bismuth made the alloys too brittle to be useful as solders for most purposes. Bismuth is added in small quantities, however, to solders for some special purposes.

Alloys Containing Zinc

As some of the cadmium alloys recommended in the literature² for use as solders contained various amounts of zinc, a number of alloys containing zinc were studied. The addition of small amounts of zinc (1.5 to 2.0 per cent.) to lead-cadmium or lead-tin-cadmium solders lengthens the solidification range and lowers the final solidification temperature slightly, decreases the tendency to oxidation, and tends to give soldered joints of greater strength and reliability. If larger amounts of zinc are added to an alloy containing lead the excess zinc merely forms a separate layer above the alloy, since zinc is only slightly soluble in molten lead at soldering temperatures.

TABLE 2.—*Solidification Ranges of Zinc-containing Alloys Studied*

Code Letter	Composition				Total Solidification Range, °C.
	Pb	Sn	Cd	Zn	
M	90.8		7.7	1.5	274-247
P ^a	87.5		7.5	5.0	275-247
AD ^a	30.8	35.2	22	12	158-136
AE		53	38	9	188-157
AF ^b			80	20	263
AG			60	40	307-263
AH	39.4	39.4	19.2	2	165-136
AJ	78.8		19.7	1.5	239
AK	56.9	16.7	24.5	2	206-136
AL	63.7	8.8	25.5	2	220-136
AM	73.5	2.9	21.6	2	231-136

^a Most of the zinc in alloys P and AD was insoluble and remained as a solid, at temperatures below its melting point, above residual alloys which had the solidification ranges given.

^b Cadmium-zinc eutectic.

² C. W. Hill: Solders and Substitutes for Lead-tin Solders. *Met. Ind.*, N. Y. (1918) 16, 412.

Zinc alloys in all proportions with cadmium alone, however, and also with tin-cadmium mixtures. Zinc-cadmium alloys offer promise of being suitable solders for certain purposes where they are to be subjected to temperatures, in use, at which tin-lead or tin-lead-cadmium solders would melt or weaken.

Solidification data concerning the zinc alloys studied are given in Table 2.

Final Solidification Temperatures

The temperatures of final solidification of the various alloy systems studied in this investigation are:

SYSTEM	FINAL SOLIDIFICATION POINT, DEGREES CENT.
Cadmium-zinc.....	263
Lead-cadmium.....	249
Lead-cadmium-zinc.....	241
Lead-tin.....	181
Tin-cadmium.....	176
Tin-cadmium-zinc.....	157
Lead-tin-cadmium.....	145
Lead-tin-cadmium-zinc.....	136

TENSILE-STRENGTH TESTS ON SOLDERED JOINTS

The tensile strength of the solder alloys studied was tested in two different ways: (1) by measuring the tensile strength of soldered joints between various metals made with the alloys, and (2) by measuring the tensile strength of the alloys themselves, in test pieces of standard shape. The first method was relied on to the greater extent because it approximated actual conditions of use more closely than the second.

Only a few of the alloys were tested by the second method. Because of their softness and tendency to flow under applied stress, the figures obtained for tensile strength of standard test pieces varied with the rate of application of the load and could not be checked closely even when conditions were kept as constant as possible. All the cadmium solders tested in this manner had tensile strengths approximately equal to or better than ordinary tin-lead solders.

The soldered joints used for testing tensile strength according to the first method were lap joints made between the ends of strips of copper, brass, or tin plate, 1 in. wide and 3 in. long. The joints were lapped 0.25 in. Zinc chloride flux was used in nearly all cases but rosin-alcohol flux was also tried and seemed to give as good results as zinc chloride.

Ordinary hand-soldering methods were used in making the joints. The strips were well tinned at the ends to be joined and then sweated together, bubbles or foreign matter being carefully excluded.

The strips were then placed in a hand-operated tensile-testing machine and the ultimate tensile strength of the joint was measured. At first

test pieces of 22-gage sheet metals were tried, but these were found too light and 16-gage was used.

In Table 3, the average joint strength of copper and brass pieces represents at least six test pieces. Three test pieces of tin-plated sheet iron were used.

TABLE 3.—Average Tensile Strength of Soldered Joints

Code Letter	Composition, Per Cent.				16-gage Brass		16-gage Copper		16-gage Tin Plate	
	Pb	Sn	Cd	Zn	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a
A	40	40	20		1705	96.4	1350	100.4	1622	103.6
B	50	50			1769	100.0	1345	100.0	1680	100.0
C	80	10	10		1322	74.7	982	73.0	1307	77.8
D	75	15	10		1359	76.8	979	72.8	1502	89.4
E	85	5	10		1397	79.0	912	67.8	1445	86.0
F	90		10		1555	87.9	1092	81.1	1513	90.0
G	25	75			1692	95.6	1180	87.7	1493	88.9
H	50		50		1790	101.2	1223	90.9	1465	87.2
J	70		30		1775	100.4	1240	92.2	1612	95.9
K	25	50	25		1663	94.0	1358	101.0	1693	100.8
L	91.5		8.5		1470	83.1	1180	87.7	1497	89.1
M	90.8		7.7	1.5	1618	91.5	1040	77.3	1300	77.3
Q	32	50	18		1884	106.5	1341	99.7	1730	103.0
R	80		20		1797	102.1	1330	99.4	1465	87.2
S		70	30		1830	103.5	1372	101.9	1768	105.3
V	58	17	25		1647	93.0	1260	93.6	1695	100.8
W	65	9	26		1685	95.3	1314	97.6	1650	98.2
X	75	3	22		1703	96.2	1245	92.5	1610	95.8
Y	60	40			1604	90.7	1368	101.7	1650	98.2
AB	54	46			1617	91.4	1162	86.4	1812	107.8
AD	30.8	35.2	22	12	1930	109.1	1460	108.5	1632	103.0
AE		53	38	9	1832	103.5	1550 ^b	115.3	1958	116.5
AF			80	20	1977	111.8	1680 ^b	125.0	1805	107.5
AG			60	40	1762	99.6	1480 ^b	110.0	1710	101.7
AH	39.2	39.2	19.6	2	1878	106.2	1363	101.3	1792	106.6
AJ	78.8		19.7	1.5	2020	114.2	1453	108.0	1638	97.5
AK	56.9	16.7	24.5	2.0	1750	98.9	1182	87.9	1628	96.9
AL	63.7	8.8	25.5	2.0	1835	103.7	1213	90.1	1665	99.1
AM	73.5	2.9	21.6	2.0	1878	106.1	1343	99.9	1748	104.0

^a Half and half lead-tin.

^b Copper strip failed.

Table 4 shows a comparison of the tensile strengths of joints made with solders containing zinc and with similar solders not containing zinc. It will be noted that in all but a few cases the solders containing zinc made the strongest joints. For convenience the zinc-containing solder is given first and the solder similar to it without zinc is given next. The zinc-containing solders which are not similar to any other solder studied have been placed at the bottom together with lead-tin solders included for comparison.

TABLE 4.—*Zinc Solder Comparison—Average Tensile Strength of Joints*

Code Letter	Composition, Per Cent.				16-gage Brass		16-gage Copper		16-gage Tin Plate	
	Pb	Sn	Cd	Zn	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a	Av. Tens. Strength, Lb.	Per Cent. Compared with Half and Half ^a
M	90.8		7.7	1.5	1618	91.5	1040	77.3	1300	77.3
L	91.5		8.5		1470	83.1	1180	87.7	1497	89.1
AH	39.2	39.2	19.6	2.0	1878	106.2	1363	101.3	1792	106.6
A	40	40	20		1705	96.4	1350	100.4	1622	103.6
AJ	78.8		19.7	1.5	2020	114.2	1453	100.0	1638	97.5
R	80		20		1797	102.1	1330	99.4	1465	87.2
AK	56.9	16.9	24.5	2.0	1750	98.9	1182	87.9	1628	96.9
V	58	17	25		1647	93.0	1260	93.6	1695	100.8
AL	63.7	8.8	25.5	2.0	1835	103.7	1213	90.1	1665	99.1
W	65	9	26		1685	95.3	1314	97.6	1650	98.2
AM	73.5	2.9	21.6	2.0	1878	106.1	1343	99.9	1748	104.0
X	75	3	22		1703	96.2	1245	92.5	1610	95.8
AD	30.8	35.2	22	12	1930	109.1	1460	108.5	1632	103.0
AE		53	38	9	1832	103.5	1550 ^b	115.3	1958	116.5
AF			80	20	1977	111.8	1680 ^b	125.0	1805	107.5
AG			60	40	1762	99.6	1480 ^b	110.0	1710	101.7
B	50	50			1769	100.0	1345	100.0	1680	100.0
Y	60	40			1604	90.7	1368	101.7	1650	98.2
AB	54	46			1617	91.4	1162	86.4	1812	107.8

^a Half and half lead-tin.^b Copper strip failed.

TESTS OF CADMIUM SOLDERS IN COMMERCIAL SOLDERING OPERATIONS

The laboratory investigation that has been described showed cadmium solders to be entirely satisfactory for hand soldering, but can manufacturers, who use the largest amounts of solder alloys, employ machines for most soldering operations. Accordingly arrangements were made with can manufacturers to try out cadmium solders in their plants.

The machines for the manufacture of the common sizes of tin cans have been brought to a high state of mechanical perfection. In making the ordinary round cans used as food containers, for example, the output may be as high as 300 cans per minute per machine. Needless to say these machines have been developed as a result of long experience with lead-tin solders, and the arrangements for heating the joints to be soldered, putting on the solder, and cooling the finished cans are all carefully correlated to suit those particular solders, and the machines are supervised by men who have had long experience with the behavior of those solders.

The use of cadmium solders in those machines, because of their different solidification range and final solidification temperature, would require a different adjustment between conditions of heating, cooling, and other controlling factors, and considerable experience in the use of cadmium

solders would probably be required to get the proper adjustment for best results.

Therefore, although some tests were made with cadmium solders in these machines, it was felt that the best field for the introduction of such solders was in certain special soldering operations where their peculiar properties would give them marked advantages over straight lead-tin solders and where conditions as to temperature, manipulation, and cooling could more easily be varied at the will of the operator.

An example of such special soldering operations is the soldering of lithographed cans. The lithographing on these cans is easily scorched and in soldering them with lead-tin solders there is always some discoloration of the lithographing near the seam, even with the most careful work. When cadmium solders having a composition close to that of the ternary lead-tin-cadmium eutectic are used for this operation the soldering may be done at a lower temperature, because of the lower solidification point of these solders, and discoloration of the lithographing is entirely avoided. As a result of our tests of cadmium alloys for this purpose, they are now having an extended trial in regular operation at a large factory.

It is thought that there may also be a special field for the binary cadmium-zinc and cadmium-lead alloys which have final solidification temperatures considerably higher than that of binary tin-lead alloys, as solders for use in apparatus which is likely to be subjected during use to temperatures at which tin-lead solders would soften or melt. Tests of these alloys for such use are being made by electrical manufacturing companies but reports of their tests had not been received when this paper was written.

SELECTING A CADMIUM SOLDER FOR A PARTICULAR PURPOSE

Many factors must be considered in the selection of a cadmium solder of the best composition for any particular purpose, depending on the conditions under which the soldering is to be done and the use to which the soldered article is to be put. Important among these factors are solidification range and final solidification temperature, strength, quality of "wetting" the metals to be joined, tendency to oxidize while molten, and cost.

The solidification range and final solidification temperature of any alloy of the lead-tin-cadmium system can be foretold by reference to the freezing-point diagram of Stoffel.

The results of the tests with the alloys studied in the present investigation indicate that any of the alloys of this system that are likely to be considered for use as solders can be made to give joints of satisfactory strength, the variations of tensile strength with varying composition not being sufficient to be decisive.

In so far as "wetting" properties and tendency to oxidation are concerned, the observations made in the course of this investigation point to the alloys in the region of the ternary eutectic composition as being most satisfactory. Larger percentages of cadmium than in the eutectic are likely to increase the tendency of the alloys to oxidize to an undesirable degree while molten. The "wetting" quality of the alloys falls off as their lead content increases, just as in the case of lead-tin solders, but a proportion of lead considerably above that existing in the eutectic alloy is permissible. Ordinarily, considerations of economy will dictate that as large a percentage of lead be used as may be without too greatly sacrificing other qualities desired in the solder.

SUMMARY AND CONCLUSIONS

The properties of a number of alloys of the lead-tin-cadmium system were studied with reference to the suitability of these alloys for use as solders. The tensile strength of joints made between various metals with these solders were determined in comparison with similar joints made with ordinary lead-tin solders.

The tests showed that solders containing cadmium would make joints equal in strength to joints made with lead-tin solders and that the cadmium alloys were suitable in other respects for use as solders. Similar tests made with the same alloys to which 1.5 to 2.0 per cent. zinc had been added showed that the addition of zinc in this proportion improved the properties of the alloys for this use.

In general, the investigation indicated the solders having compositions in the neighborhood of the ternary lead-tin-cadmium eutectic as being the best of the ternary alloys for most soldering work, though compositions varying rather widely from this may be more desirable for certain purposes.

As regards the introduction of cadmium solders into large-scale commercial soldering work, it was decided that the best place to make a start was in the operations in which properties peculiar to cadmium solders, such as low solidification temperature, give them a special advantage over lead-tin solders. Efforts in this direction are bearing fruit.

A very considerable and dependable market for cadmium solders already exists.

SELECTED BIBLIOGRAPHY

- N. F. Budgen: Cadmium, Its Metallurgy, Properties and Uses, 147-149, 167, 169, 175, 181-186, 189. New York, 1924.
Solders Containing Cadmium. *Metal Ind.*, N. Y. (1925) **23**, 104.
G. K. Burgess and R. W. Woodward: Bronzes, Bearing Metals and Solders. *Trans.* (1919) **60**, 175; Cadmium as a Tin Substitute, 181.
Conservation of Tin in Bearing Metals, Bronzes, and Solders. Bur. of Stds. *Tech. Paper* 109 (1919) 8-9.

- R. B. Deeley: Zinc Cadmium Alloys, a Note on Their Shear Strengths as Solders, *Jnl. Inst. of Metals (British)* (1925) **34**, 193.
- C. W. Hill: Solder without Tin. *Chem. & Met. Eng.* (1918) **19**, 170, 660.
Solders and Substitutes for Lead-tin Solders. *Met. Ind.*, N. Y. (1918) **16**, 412.
- C. E. Siebenthal: The Cadmium Supply of the United States. *Trans.* (1919) **60**, 185; Cadmium Solder, 190, with discussion, 190-192.
- H. C. Urquhart: The Uses of Cadmium. *Proc. Australasian Inst. Min. & Met.* (1923) **52**, 207-222.

DISCUSSION

G. E. DALBEY, East Berlin, Conn.—Some time ago a practical tinner said it was his experience that cadmium solder was a desirable solder for use on galvanized sheet but he did not think much of it on tin sheet. He could not say why; he just believed that was so from some observations, but he could not tell definitely what they were.

C. S. SMITH, Waterbury, Conn. (written discussion).—The remarks of the previous speaker that cadmium solders are superior to lead-tin ones when soldering galvanized iron, I can confirm, although I have not been able to advance a satisfactory theory to account for this.

As Mr. Swartz remarks, the literature contains few references to the lead-tin-cadmium alloys, which possess properties worthy of more attention. I have been doing some work on this system and offer the following comments.

The terms "alloying," "wetting," "flowing," and "capillary action" are used in the paper almost as if they were synonymous. "Alloying" denotes the formation of a definite compound, solution or mixture of the base metal with the solder, and, while this usually occurs, it is not an essential part of the formation of a soldered joint. "Wetting," on the other hand, is concerned with surface adhesion and probably depends far more on the flux than on any characteristic of the solder itself. If the surface is perfectly clean, the solder will wet it rapidly, just as water will wet a perfectly clean metal surface.³

The smaller its surface tension and the surface energy of the metal-solder interface, the greater the ability of a solder to spread on a clean metal surface which has not previously been wet. Once the surface has been wet, however, the ease and speed with which the metal can spread over a surface and penetrate crevices depends directly on the surface tension, which then acts in the same way as when lifting a column of liquid in a capillary tube against the action of gravity. It appears probable that the latter action is more important from a practical standpoint than the former, and it is the result of experience that solders with a high surface tension are the most convenient to use.

The surface tension of cadmium is greater than that of tin and much greater than that of lead. Although no measurements have been reported on the ternary system, one can assume that, except at the extreme corners of the diagram, linear relations hold approximately, and consequently the addition of cadmium to a tin-lead solder not only lowers the melting point but simultaneously increases the surface tension, and therefore the running properties of the alloy. It is this fact which enables us to use without difficulty cadmium solders containing very high percentages of lead.

It is to be regretted that Mr. Swartz did not determine the melting points of the alloys with greater accuracy. The writer has himself determined, with an accuracy believed to approach $\pm 1^\circ$ C., the freezing points of the alloys containing more than

³ Dean and Wilson [*Ind. & Eng. Chem.* (1927) **19**, 1312] show that the action is actually more complex than this. The presence of hydrochloric acid seems to be necessary for rapid wetting, and probably acts by displacing the layer of adsorbed air.

50 per cent. lead and less than 20 per cent. cadmium. Cooling curves were taken on accurately weighed out 100-gm. samples, melted under an oil of high boiling point. The rate of cooling was 3° to 6° C. per min. A bare iron-constantan thermocouple was used, in conjunction with a potentiometer reading to 0.001 mv. The couple was calibrated against the freezing points of lead (327.4° C.) and tin (231.8° C.) and boiling water (100° C. at 760 mm.). The alloys were made from commercially pure lead and cadmium and pure tin (99.965 per cent.). Fig. 2 shows the liquidus isothermals deduced from the results. These differ but slightly in position from the ones given by Stoffel.⁴ On account of the rather wide spacing of the alloys in the part of the diagram with less than 80 per cent. lead the location of the isothermals in this area is probably not quite as accurate as above stated.

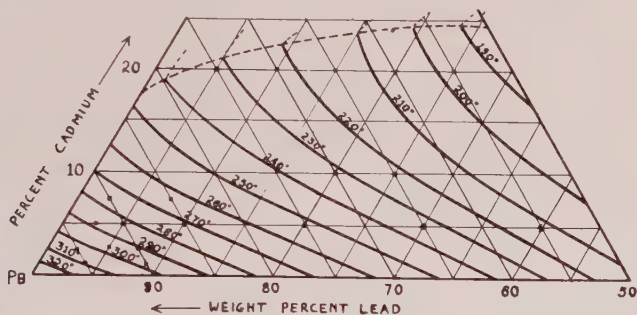


FIG. 2.—LIQUIDUS ISOTHERMALS OF THE LEAD-CADMIUM-TIN SYSTEM.

Tensile tests on joints made between pieces of copper, brass and steel rod and strips of galvanized and plain Armco iron showed a much greater variation between the different classes of solder than Mr. Swartz observed. This is shown in Table 5.

TABLE 5.—*Mechanical Properties of Solders and Soldered Joints*

No.	Composition				Cast Alloy ^a			Soldered Joints	
	Pb, Per Cent.	Cd, Per Cent.	Sn, Per Cent.	Zn, Per Cent.	Tens. Str. Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Reduction of Area, Per Cent.	Copper Rod Tens. Str. Lb. per Sq. In.	Galv. Iron Strip Shear Str. Lb. per Sq. In.
2	70	10	20		6,595	55.0	55.0		2,350
3	50		50		6,880	36.3	60.0	24,750	2,440
7	60	20	20		9,475	18.3	37.5	20,050	2,400
9	32	18	50		9,860	82.5	99.9 ^b	22,000	2,440
23		40		60	22,400	4.8	12.0	27,150	4,840 ^c
26		80		20	22,250	19.3	34.0 ^c	33,250	5,550 ^c

Each figure is the average of two or more results.

^a Speed of loading $\frac{3}{8}$ in. per minute.

^b Drew down to a point.

^c Ungalvanized strip.

This table includes the results only of a few typical compositions selected from the whole range studied. The tests on the cast alloys were performed on test pieces

⁴ A. Stoffel: *Op. cit.*

machined from $\frac{1}{2}$ in. dia. chill-cast bars. The parallel portion was $2\frac{1}{2}$ in. long, and 0.436 in. dia. The joints in copper rod were made between two pieces 0.314 in. diameter, with carefully turned flat ends. The solder layer, therefore, was tested in pure tension. The values for the strip joints, which were $\frac{1}{2}$ in. wide and made with $\frac{1}{2}$ in. overlap, are the only ones which are at all comparable with those made by Mr. Swartz, who used an overlap of the same area, although 1 in. wide by $\frac{1}{4}$ in. overlap. The results in Table 3 were expressed as "tensile strength-pounds." This presumably is the actual breaking load of the joints and would have to be divided by the area of the overlap to obtain the actual shear strength of the soldered area in pounds per square inch. The results of Mr. Swartz are in all cases very much higher than those of the present writer, a discrepancy which can hardly be due to the different shape of test piece. Perhaps a comparison is hardly justified because of the fact that Mr. Swartz used tin-coated steel instead of the plain and galvanized stock of the

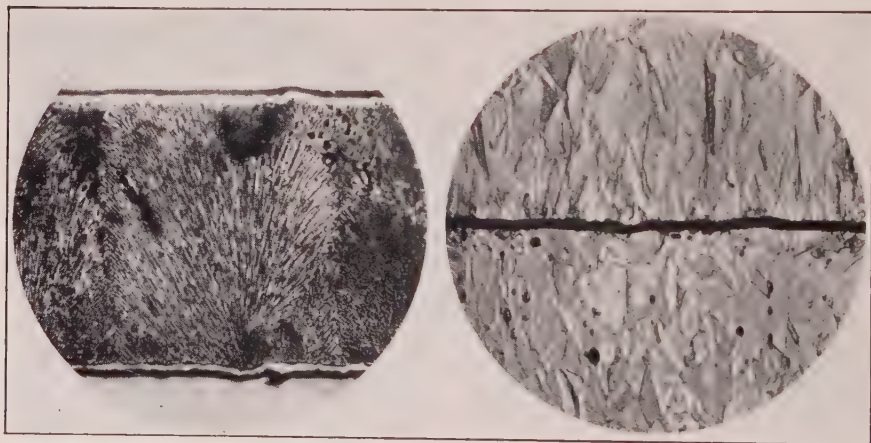


FIG. 3.—SOLDERED JOINT IN COPPER MADE WITH 17.5 PER CENT. ZINC, 82.5 PER CENT. CADMIUM SOLDER. $\times 500$.

FIG. 4.—CROSS-SECTION OF A BROKEN JOINT. $\times 500$.

(Figs. 3 and 4 are reduced to approximately $\frac{2}{3}$ original scale, original magnifications given.)

writer. This would tend to favor the lead-tin solders rather than the cadmium-zinc alloys.

Impact tests on the joints showed them to be extremely weak. The test piece employed was a round butt joint, 0.314 in. dia., supported on knife edges, each 25 mm. from the actual joint, at which point the falling pendulum struck. The strongest joints tested broke at 0.105 kg.-m., a value so small as scarcely to be visible on the scale of the standard Charpy testing machine employed. Very crude tests made with a hand hammer showed that in general the lead-tin-cadmium solders were decidedly inferior to the straight lead-tin solders, although even joints made with the latter could be broken with extreme ease.

The use of a binary lead-cadmium alloy as a solder of intermediate melting point is rendered difficult on account of the rapid oxidation of the cadmium. The addition of a small amount of zinc, as suggested by Hill,⁵ although it prevents rapid oxidation, raises the melting point and increases the pasty range considerably, making a solder that is not convenient to use. Tin similarly prevents oxidation but rapidly lowers the

⁵ C. W. Hill: Solder Without Tin. *Chem. & Met. Eng.* (1918) **19**, 170.

melting point, and even in very small quantities gives rise to the ternary eutectic melting at 145°C .

As soft solders of rather high melting point the cadmium-zinc binary alloys are very good. The eutectic is slightly better than other compositions, but the cheaper 50-50 alloy is more suitable for general use and is almost as satisfactory. This alloy commences to solidify at 326°C . and is completely solid below 265°C . The running properties of the metal are excellent, as is to be expected from the high surface tension of both constituent metals. The joints are much stronger than those made with ordinary

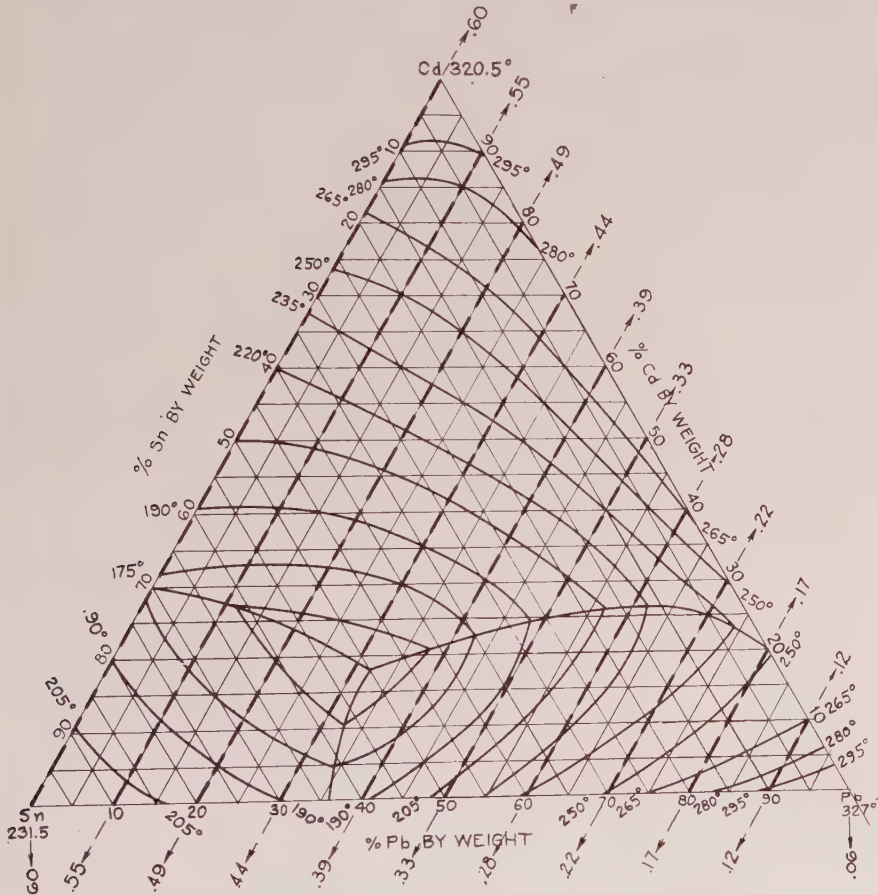


FIG. 5.—CURVES OF EQUAL COST, LEAD-TIN-CADMIUM SOLDERS.

soft solder. This is particularly so when joining steel, for when soldering copper the formation of layers of brittle compounds results in a somewhat weak joint. Fig. 3 is a photomicrograph, at a magnification of 500, of a joint made between two pieces of copper rod, using solder of eutectic composition (17.5 per cent. zinc, 82.5 per cent. cadmium). There is visible a layer of dark compound next to the copper, followed by a layer of white compound in contact with the solder itself. The boundary between the two is very distinct. If such a joint is broken, fracture will occur sharply between these two layers and will never travel other than perpendicularly through the solder. One

of the halves of the broken joint will have the layer of black compound remaining on it and the other will have the whole thickness of the solder and the layer of white compound adhering to it. Fig. 4, which is a cross-section of a broken joint, copper plated for protection during polishing, shows this well. When soldering steel, layers of compound of visible thickness are never formed and it seems to be the strength of the solder itself which determines the strength of the joint.

E. E. SCHUMACHER, New York, N. Y.—For some time past an investigation has been in progress in the Bell Telephone Laboratories to develop new solders. In the course of this study about fifty Pb-Sn-Cd alloys have been tested and certain of them have been found to possess properties that recommend them as wiping solders.

Since Dr. Schwartz barely touches upon the subject of wiping solders in his paper it seems desirable to say just a word in this connection.

We have found that the alloys of high lead content in which no binary eutectic freezes out during solidification are especially good from the wiping standpoint. For instance, an alloy containing as high as 68 per cent. lead (68 per cent. Pb, 23 per cent. Sn, 9 per cent. Cd) functions satisfactorily and our laboratory tests indicate that this alloy possesses physical properties that are comparable with those of ordinary lead-tin solder (62 per cent. Pb, 38 per cent. Sn). Tinning with this alloy is rapid, it works nicely during the wiping process, it does not oxidize excessively at 400° C. and wiped joints made with it withstand a pressure test of 30 lb. per sq. in. without leaking. Some of the advantages of this alloy over ordinary lead-tin (62 per cent. Pb, 38 per cent. Sn) solder are: (1) it has a longer cooling range, which permits the splicer more time for shaping his joint, (2) it seems to tin more easily and at a lower temperature, and (3) it is cheaper.

For conveniently showing the cost of the various binary and ternary alloys of Pb-Sn and Cd, a diagram of curves of equal cost for these alloys has been constructed (Fig. 5). From this diagram it is at once apparent that all alloys lying to the right of the 62 per cent. lead line are cheaper than ordinary solder. Further tests will have to be conducted before the value of these Pb-Sn-Cd alloys as wiping solders can be definitely appraised, but we can say now that as far as our tests have progressed certain of these alloys appear very promising.

F. H. EDWARDS, Brooklyn, N. Y. (written discussion).—I would like to ask two questions:

1. Would it not be better to call the mechanical tests on soldered joints "shear tests" instead of "tensile-strength tests?" Solders are rarely employed under straight tension loads but their shear strength is important. It is quite fitting to call the tests on the lap joints, described on page 357, "shear tests."

2. Did the authors make any attempts to control the thickness of the solder film? Crow⁶ found this to be the most important feature of a soldered joint. The thinner this film of solder, provided proper wetting or alloying with the metals to be joined, the greater the mechanical strength of the joint made. It may also be remembered that the thickness of the solder in a joint is only a few thousandths of an inch and there may easily be a variation of 50 per cent., which will considerably alter strength values.

R. S. DEAN, Chicago, Ill.—I am encouraged by the amount of interest that seems to be arising in regard to soldering. It certainly is a most important process and

⁶ T. B. Crow: Some Properties of Soft Soldered Joints. *Jnl. Soc. Chem. Ind.* (1924) **43**, 58.

Some Scientific Aspects of the Process of Soft Soldering. *Brass World* (1925) **21**, 39, 133.

one about which we do not seem to know a great deal. I was much interested in what Mr. Smith had to say about wetting. After all, what many of us are interested in with regard to solders is not how strong they are within very wide limits, because most all solder is strong enough, particularly for a certain type of electrical joint, but in how quickly we can apply it, which is a matter of how fast it will flow. I am inclined to agree with Mr. Smith that that is a function more of the flux than of the solder, although I would like to know the effect of various solders in that connection.

F. H. CLARK, New York, N. Y.—It has been stated that these lead-tin-cadmium solders are quite satisfactory for use as wiped joints. I would like to ask how the porosity of these joints compare with ordinary lead-tin solders. I am also interested in the electrical conductivity of these alloys.

E. E. SCHUMACHER.—Our data on the porosity of lead-tin-cadmium alloys are quite meager. We have found that a wiped joint made with an alloy composed of 68 per cent. lead, 23 per cent. tin and 9 per cent. cadmium withstands an air pressure of 30 lb. per sq. in. without leaking. If the percentage of lead is increased to 70, the joint is porous. Joints made with lead-tin solders withstand this pressure test satisfactorily as long as the lead content is kept below 62.5 per cent.

R. S. DEAN.—Has anyone any data on the electrical conductivity of those alloys?

F. F. COLCORD, New York, N. Y.—About 10 years ago Walter C. Smith did some work on these lead-tin-cadmium alloys as a substitute for 50-50 solder and my recollection is that the conductivity was higher than with the 50-50 lead-tin-solders.

G. E. DALBEY.—What results have been noticed in soldering or dipping radiators in the cadmium solders as compared to the lead-tin solders? With the ordinary dipping solder, say a 40-60 solder, sometimes in dipping there is a little patch on the surface of the brass that the solder has flowed around and has not covered, and in pulling that brass apart you find these bare spots. That even occurs after very careful cleaning of the brass. I wonder if the cadmium solder has more of a tendency to cover than the lead-tin solder.

O. W. ELLIS, East Pittsburgh, Pa. (written discussion).—Both zinc and cadmium are subject to allotropic change; the former undergoes transformations at 180° C. and at 300° C., the latter between 60° and 70° C. The effects on these transformation points of adding cadmium have not been investigated. There is no reason to suppose, however, that they are completely suppressed.

The question arises as to the effect of the transformations of these two metals on the mechanical properties of their alloys at high temperatures. It is not impossible that this effect may be of outstanding importance. It is open to question, therefore, whether we can say offhand that "zinc-cadmium alloys offer promise of being suitable solders for certain purposes where they are to be subjected to temperatures, in use, at which tin-lead or tin-lead-cadmium solders would melt or weaken." Preliminary tests by the writer seem to indicate a pronounced weakening at about 100° C. of joints soldered with the eutectic of this system. This may or may not be due to allotropic changes in the components of the eutectic, but it is a phenomenon that appears worthy of fuller investigation.

C. E. SWARTZ (written discussion).—My replies to Mr. Edwards are:

1. Although the tests made were in tension, an analysis of the strains shows that shearing is the greater factor in the failure.

2. In these soldering experiments, it was our purpose to approximate as nearly as possible average hand-soldering operations, therefore no attempt was made to keep the solder layer uniform in thickness. However, a firm pressure was kept on

the work until the solder film was completely solidified. The film was found to be approximately the same thickness throughout the tests.

The discrepancy between Mr. Smith's data on the strength of the soldered joints and the author's may be partly accounted for as follows:

1. The testing machine used by the author was hand-operated, so no exact figure for rate of loading can be given, although it is believed that the speed of loading was slightly in excess of 1 in. per min. Hence the results would tend to be a little higher than those of Mr. Smith.

2. The lap joint used by Mr. Smith was $\frac{1}{2}$ in. wide and $\frac{1}{2}$ in. lap, while those of the author were 1 in. wide with $\frac{1}{4}$ in. lap. In soldering there is always a certain amount of adherence of solder film to the end of the strip, adding strength to the joint. Since the width of the strip used in the author's tests was double that used in Mr. Smith's tests, the increment of strength due to this factor is double. For this reason, no attempt was made to give the strength per unit area of surface soldered, as Mr. Smith has done.

Some Peculiar Results in Hardness Tests of Lead-antimony Alloys

BY L. O. HOWARD, PULLMAN, WASHINGTON

(New York Meeting, February, 1928)

MUCH work has been done recently on the lead-antimony system¹ in connection with lead-rich alloys of commercial importance containing less than 20 per cent. antimony. Dean, Zickrick and Nix have called attention to the perpetuation in the literature of several erroneous data, such as a eutectic temperature of 228° C. at 12.5 per cent. antimony, instead of 247° at 13 per cent. The series is given as a classic example of a straight eutectiferous series in such late books as those of Heyn and Grossmann,² Jeffries and Archer,³ Guillet and Portevin,⁴ Pulsifer,⁵ Rosenhain,⁶ and Liddell,⁷ as well as the somewhat earlier works of Hofman (1918), Wang (1909), and Williams (1920). The work of Dean has definitely shown a solid solution of antimony in lead at about 2.5 per cent. antimony.

While lecturing to a class in general metallurgy at the University of Idaho, the writer had the students prepare a series of lead-antimony alloys for the purpose of illustrating methods of thermal analysis. Proper proportions of powdered antimony (sold as C.P.) and test lead were mixed and melted in graphite crucibles under a reducing cover. Cooling

¹ R. S. Dean: The Lead-antimony System. *Jnl. Amer. Chem. Soc.* (1923) **45**, 1683.

R. S. Dean, W. E. Hudson and M. F. Fogler: The Lead-antimony System, II. *Ind. & Eng. Chem.* (1925) **17**, 1246.

R. S. Dean, Lyall Zickrick and F. C. Nix: The Solidus Line in the Lead-antimony System and Hardening of Lead Alloys. *Trans.* (1926) **73**, 505.

Earle E. Schumacher and Foster C. Nix: The Solidus Line in the Lead-antimony System. *Proc. Inst. Met. Div., A. I. M. E.* (1927), 195.

² E. Heyn and M. A. Grossmann: *Physical Metallurgy*, 13. J. Wiley & Sons, Inc., New York, 1925.

³ Zay Jeffries and R. S. Archer: *The Science of Metals*, 296. McGraw-Hill Book Co., Inc., New York, 1924.

⁴ L. Guillet and A. Portevin: *Introduction to the Study of Metallography and Macrography*, 244. Bell, London, 1922.

⁵ H. B. Pulsifer: *Structural Metallography*, 45. The Chemical Publishing Co., Easton, Pa., 1924.

⁶ W. Rosenhain: *Introduction to Physical Metallurgy*. D. Van Nostrand Co., New York.

⁷ D. M. Liddell: *Handbook of Non-ferrous Metallurgy*, 16. McGraw-Hill Book Co., Inc., New York, 1926.

curves were taken with a rare-metal pyrometer, the alloys were remelted and cast in iron molds, as buttons weighing 100 to 200 gm. Specific gravities were determined and hardness tests made by a modification of the Brinell test devised by the writer. The antimony button (assumed hardness 55) and the one next lower in antimony content were placed in a vise with a 10-mm. Brinell ball between them and pressure applied slowly, taking care to release the pressure suddenly as it approached the maximum. The diameters of the impressions were carefully measured and the depth h of the impression calculated. The unknown hardness was then readily calculated, being inversely as h . Repeating the test with the alloy of which the hardness has just been determined as the known and the alloy next lower in antimony as the unknown, and continuing through the series, the hardness of lead was found to be 5.17. Jeffries and Archer⁸ give the hardness of chill-cast lead as 5.1 to 5.4. It seems probable, therefore, that the numbers given in Table 1 are correct for the upper surfaces of the particular alloys, since each hardness number is tied into the series in a manner impossible with the usual Brinell test.

TABLE 1.—*Brinell Tests on Lead-antimony Alloys Made at University of Idaho*

Per Cent. Antimony.....	100	85	70	50	30	12.5	5	0
Brinell Number.....	55	41.44	30.67	15.43	23.77	21.06	17.67	5.17

A year ago, at the South Dakota School of Mines, the writer had a similar set of alloys made from metals as pure as could be obtained commercially. Brinell tests made in a standard machine gave the irregular curve shown in Fig. 1, and were at first supposed to be due to possible erroneous determinations. This objection does not apply to the Idaho tests, which show somewhat similar irregularities. The low hardness numbers for 40 to 50 per cent. antimony alloys cannot be explained on the ground either of experimental errors or coincidence.

Among causes considered was segregation, the tendency of certain lead-antimony alloys to segregate on slow cooling being the classic example chosen by most authors to illustrate the phenomenon of segregation. The alloys were stirred before casting and chill cast at a temperature just safely above the solidification point. The equilibrium diagram (not reproduced) shows no abnormalities. Microscopic examination of sections cut to show the structure from top to bottom and center to outside shows no appreciable segregation except in one or two specimens containing less than 30 per cent. antimony. Occasionally slight coarsening toward the center was noted. The microscope, then, gave no positive assistance in determining the cause of the peculiar shape of the hardness curve.

⁸ *Op. cit.*, 176.

Although as late as 1923 Dean⁹ postulated the occurrence of a compound Pb_4Sb at 12.5 per cent. antimony, later diagrams by him appear to leave this compound unconsidered. Our diagram shows no evidence of a compound although it is possible that one may have formed after solidification, which was not detected on our rather rough cooling curves. Sir William Roberts-Austen states,¹⁰ "Compounds are frequently harder than the constituent metals, but in a few cases are softer, for example, Cu_2Sb is softer than antimony." If this is true, it is possible that there

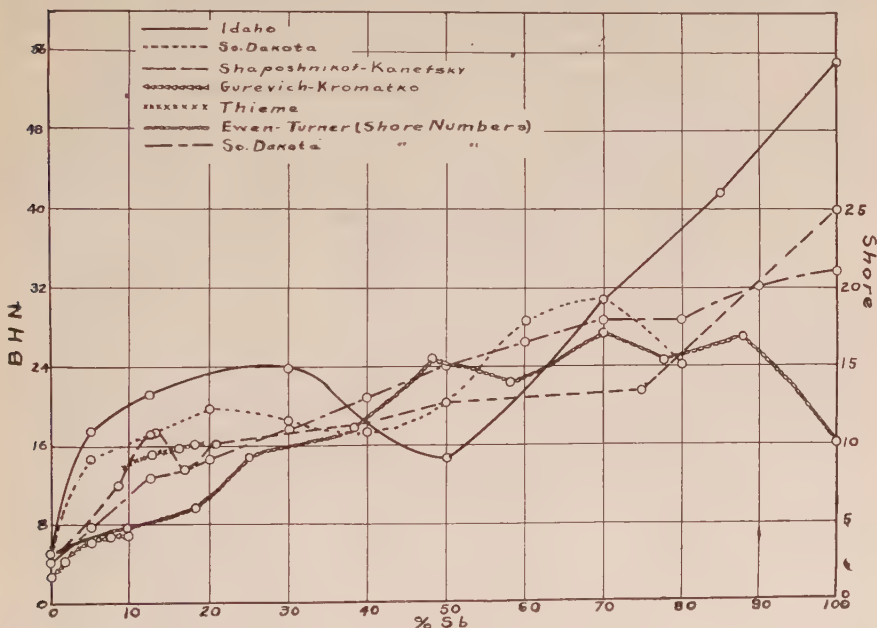


FIG. 1.—VARIATIONS IN HARDNESS OF LEAD-ANTIMONY ALLOYS REPORTED BY DIFFERENT INVESTIGATORS.

is a soft compound of antimony and lead near 40 to 50 per cent. antimony as yet undetected, which forms after solidification, and is, therefore, not evident in the usual equilibrium diagram, due to lack of careful experimentation in this region, and which more careful work such as that done by Dean and associates on the lead-rich end might reveal. Fig. 1 shows curves and parts of curves from several authors, and for comparison, the Idaho and South Dakota curves. The discrepancies are noteworthy. In the lead-rich end they may be attributed to tests on alloys that have had dissimilar treatments. The literature does not commonly give the condition of the alloy. Some are doubtless annealed,

⁹ *Jnl. Amer. Chem. Soc.* (1923) **45**, 1687.

¹⁰ Sir William Roberts-Austen: *An Introduction to the Study of Metallurgy*, 229, C. Griffin & Co., Ltd., London, 1920.

giving low hardness, others chill cast, giving greater hardness, and others aged. Dean¹¹ has demonstrated that annealing at 238° followed by quenching and aging for 10 or 11 days gives a hardness of 20.5 for a 10 per cent. antimony alloy and 18.6 for one containing 5 per cent. antimony. Fig. 2 is plotted from Dean's results and our chill-cast interpolation, and shows how discrepancies in hardness numbers at this end of the series may have gotten into the literature.

Chill casting alone may be sufficient to account for high hardness. Jeffries and Archer¹² give the hardness of the eutectic when chill cast

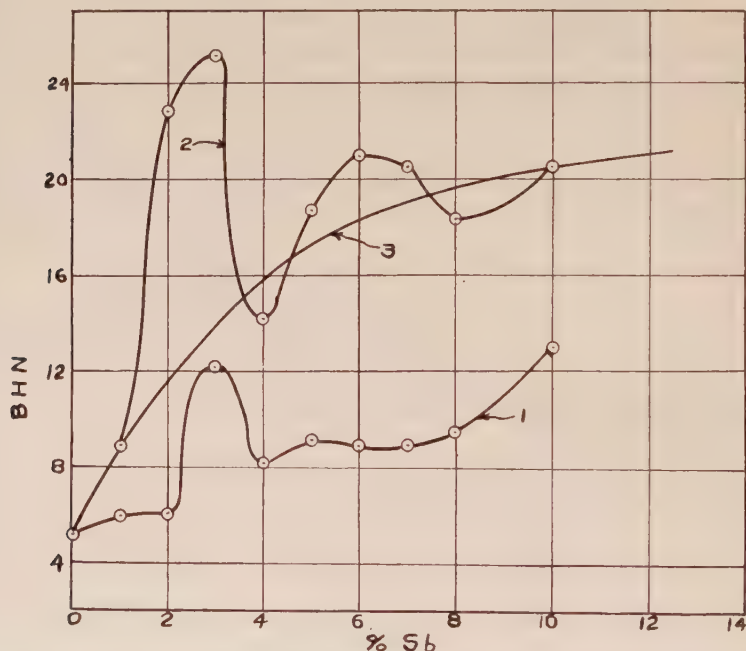


FIG. 2.—HARDNESS CURVES OF VARIOUSLY TREATED LEAD-ANTIMONY ALLOYS.

1. Heated to 238° C. and quenched (after Dean). 2. Aged eleven days (after Dean). 3. Chill cast.

as 20.36, which is close to that of our alloy containing 12.5 per cent. antimony.

Close agreement between specific gravities as determined and as calculated serves as a check on composition in the absence of analysis, eliminating the possibility of the low hardness at 50 per cent. antimony being due to excessive volatilization of antimony during preparation of the alloys, thermal analysis, and cooling. It is not likely that impurities would account for the softness of the 50 per cent. alloy.

¹¹ *Trans.* (1926) **73**, 524.

¹² *Op. cit.*, 346.

SUMMARY

1. Hardness tests made at the University of Idaho on a series of chill-cast antimony-lead alloys show a decided drop in hardness of alloys in the vicinity of 50 per cent. antimony; a similar drop appears at 40 per cent. antimony in a similar series tested at the South Dakota School of Mines.

2. Discrepancies in hardness numbers reported by various authors are doubtless due to the different treatment given, as indicated by curves showing the difference in hardness of quenched and aged specimens (from results of Dean).

3. The possibility of a soft compound of lead and antimony in the vicinity of 50 per cent. antimony, forming after solidification, must be considered and might be revealed by more careful work. Roberts-Austen's statement that there is a soft compound of copper and antimony may be indicative of a similar compound of lead and antimony.

DISCUSSION

G. O. HIERS, Brooklyn, N. Y. (written discussion).—Some years ago we hardened some commercial antimonial lead sheet. The metal was considerably worked when produced, as the thickness was reduced more than 95 per cent. in rolling. Our specimens were hardened by heating to 235° C. and quenching in water. On aging, the Brinell hardness of these specimens varied as shown in Table 2.

TABLE 2.—*Effect of Aging on Hardness of Commercial Antimonial Lead Sheet*

Dates.....	5/21/20	5/24/20	6/3/20	10/2/20	2/18/28
Age after heat treatment.....	1 Day	4 Days	14 Days	104 Days	7¾ Yrs.
4 per cent. Sb, untreated.....	8.1			8.6	8.3
4 per cent. Sb, heat treated.....	24.3	24.3	22.0	22.8	18.4
6 per cent. Sb, untreated.....	8.6			9.0	9.0
6 per cent. Sb, heat treated.....	25.5	26.0	23.1	21.2	17.4
8 per cent. Sb, untreated.....	9.5			10.1	10.0
8 per cent. Sb, heat treated.....	26.3	26.5	25.3	24.0	19.9

These findings are consistent with the predictions of Dean and co-authors.¹³

R. S. DEAN, Chicago, Ill.—Mr. Howard has suggested particularly that the alloys around 50 per cent. antimony may show some peculiar characteristics. At one time I was convinced that there were compounds in that system but one by one the various things which might be said to support the idea have been removed.

It was thought for many years that alloys of the eutectic composition of around 15 or 20 per cent. antimony expanded on solidifying. However, Fogler actually

¹³ R. S. Dean, L. Zickrick and F. C. Nix: *Op. cit.*

measured that and found they did not expand on solidifying. Various people have found various hardness maxima pretty well over this system, but there are two factors that affect this hardness maxima and minima which have nothing to do with compound formation, which we have to watch carefully—one, the hardening phenomena, and the other, simply the structural characteristics of the eutectic; that is the lead-antimony eutectic, which can be hardened depending on the degree of dispersion between the lead-antimony constituents.

So, while Mr. Howard has rightly suggested that we do not know very much about the center portion of that system, I do not believe that the evidence for a compound there is very good.

G. E. DALBEY, East Berlin, Conn.—Mr. Dean called attention to the work of Fogler, who found that antimony-lead alloys did not expand on solidifying. Do you know whether lead-tin-antimony alloys will expand on solidifying? Type metals are built up with the idea that they will expand on solidifying and give sharp edges and corners.

R. S. DEAN.—The question of type metals, that is the complex type metals, is one we have not gone into experimentally. A very sharp casting can be made with a 20 per cent. antimony alloy, which was once used in certain classes of type-metal work, but the problem of getting a sharp casting has been largely erroneously traced, I believe, to the expansion on solidification. Those alloys do not contract as much as some other alloys, and in certain instances they may even contract less than the mold by which means they have effectively expanded. But I am inclined to believe it is more a matter of viscosity and surface tension at the time of solidification, because 15 or 20 per cent. antimony alloys certainly do not expand on solidifying; they contract by an amount that would be expected from the contraction of antimony and the contraction of lead.

G. O. HIERS.—Practically all type metals do undergo an appreciable volume shrinkage while solidifying. In most cases, this shrinkage is progressive, proceeding from the face of the type inward and toward the gate. Therefore, since the face of the type solidifies first, the amount of shrinkage upon solidification is not a matter of great importance. This shrinkage at the face is filled or offset by remaining molten metal from behind. I believe that the perfect casting of delicate type requires a metal having relatively low surface tension and that the shrinkage is a minor matter.

L. O. HOWARD (written discussion).—The dip in the hardness curve in the vicinity of 50 per cent. antimony remains unexplained. Hardening phenomena and structural characteristics of the eutectic, as Dean brings out, are sufficient explanations of the differences in the various curves that have been published. I had hoped, in presenting this paper, that some explanation of the dip would be forthcoming. The discussion is not favorable to the occurrence of a compound there, but the evidence against it is not given. I must admit that supporting evidence for a compound is not great, but, to date, the compound idea is the only one that has been advanced, and cannot be summarily dismissed without further experimentation or the bringing forward of more evidence than has yet been made public. If my paper will stimulate someone to careful investigation of this phenomenon, one of its purposes will have been served. I take it that the hardness curve of chill-cast antimony-lead alloys that I have published is accepted as substantially correct, and will serve as basis for further study of the whole range.

The Cause of Translation Striae and Translation Strain-hardening in Crystals

BY M. J. BUEGER,* CAMBRIDGE, MASS.

(New York Meeting, February, 1928),

POSSIBLY the most puzzling features observed during a single-crystal deformation test are the appearance of slip striae on the surface of the crystal and the strengthening of the specimen.¹ While the first phenomenon is mainly of theoretical interest, the latter is fundamental to all strain-hardening and cold-working processes in which the deformation occurs by translation.

The plastic deformation of crystals has received considerable discussion² and need not be reviewed here in any great detail. It has been observed, essentially, that after a certain amount of initial stress is applied, the surface of the crystal becomes covered with sets of parallel striae or rings which appear to divide it into thin slabs or slip blocks.³ The striae are the traces of rational crystallographic planes along which shearing movements are localized, these movements providing the strain which accompanies stress applied beyond pure elasticity. As deformation under the applied stress proceeds the slip blocks shear past one another, although the essentially single-crystal character of the specimen is unimpaired. All of the shearing apparently takes place in the immediate vicinity of the original slip striae without the appearance of new planes of movement.⁴ Since each increment of strain is attended by an increased stress requirement to continue the deformation, the crystal strengthens during the process.

* Instructor, Department of Geology, Massachusetts Institute of Technology.

¹ Samuel L. Hoyt: Plastic Deformation of a Zinc Single Crystal. *Proc. Inst. of Metals Div., A. I. M. E.* (1927) 118, Fig. 2.

Orlando E. Romig: Preparation of Metallic Single Crystals and Twinning in Zinc and Zinc Single Crystals. *Idem.*, 101, Fig. 9.

² For recent discussions see: J. T. Norton and B. E. Warren: Plastic Deformation of Metals. *Proc. Inst. of Metals Div., A. I. M. E.* (1927) 350.

C. H. Mathewson and Albert J. Phillips: Plastic Deformation in Coarse-grained Zinc, *Idem.*, 143.

Orlando E. Romig: *Op. cit.*

Samuel L. Hoyt: *Op. cit.*

³ See photographs shown by Hoyt: *Op. cit.*, 120, Fig. 4; and 123, Fig. 6.

⁴ Hoyt: *Op. cit.*, 125.

With the simple lattice in mind, it can be shown that, under an applied stress, a given crystal should deform in a definite fashion. The direction of the shearing movement will be parallel to rows of consecutively like-charged atoms, and the planes between which such movement occurs will be the family of planes containing this translation direction which has the greatest interplanar spacing.⁵ Herein lies the discrepancy between inference and observed behavior. There appears to be no reason why every possible pair of planes of the family should not shear equally and simultaneously past one another, while, as a matter of experimental fact, the great majority of planes do not slip at all, the total deformation being accounted for by the select few in the immediate vicinity of the striae. Hoyt, in discussing zinc single-crystal deformation behavior, pointedly asks the question, "In the zinc crystal, why is it that, of all the basal planes available for slip, so few are used, and what determines the selection?"⁶ It is the purpose of the present paper to develop a working hypothesis which will account for this feature as well as for strain-hardening, with which it is closely linked.

DISTRIBUTION OF SLIP STRIAE

Examination of a deformed crystal will reveal the fact that slip striae are not distributed at random. It is true that they are not always equally spaced—and the supposed reason for this will presently appear—but they display a certain periodic arrangement. Moreover, sharp serrations, rigidly delimiting slip blocks, do not necessarily accompany deformation. Hoyt found that the surface of a deformed zinc crystal showed no markedly stepped appearance but remained relatively smooth despite the appearance of striations.⁷ The writer has noticed the same conditions in some deformed ore-mineral single crystals. The hypothesis immediately suggests itself that there is a certain periodic difference in character of the atomic planes, the consequences of which manifest themselves during deformation; certain sections of the crystal—those which constitute the slip blocks—are hard and rigid, resisting deformation from the outset, while others—the slip striae regions—are relatively soft and weak, and these sections grade into one another without abrupt changes in character. This hypothesis, being essentially a description of observed conditions, must have a strong claim to truth; the only uncertainty involved is whether the periodicity is indeed true periodicity, however complex, or merely an adventitious likeness thereof.

⁵ M. J. Buerger: The Plastic Deformation of Ore Minerals—A Preliminary Investigation. *Am. Mineral.* (1928) **13**, 15-17.

⁶ *Op. cit.*, 127.

⁷ *Op. cit.*, 124.

If there is a periodic change, what causes it? It can be nothing inherent to the lattice itself, for the minute topography of the markings differs on various deformed crystals of the same species. On the other hand, when the universal hardening effects of dissolved foreign substances in solid-solution alloys are recalled, an explanation presents itself: the slip blocks may be harder by reason of their localized, dissolved impurities and the slip-striae regions softer because of their relative freedom from impurities. This possibility becomes the more plausible when one reflects that, due to the very general solubility of one substance in another, even though it be in traces, no crystal can more than remotely approach 100.0% per cent. purity.

Such an explanation calls for a discussion of solute-atom distribution in crystal lattices.

THE IMPURITY POSSIBILITY

Solute-atom Distribution

Rosenhain⁸ has shown that solid-solution crystals demand distorted solvent lattices on account of the disturbing influence of the introduced solute atoms. Since even the purest crystals obtainable are nothing more than very dilute solid solutions at best, it is obvious that this distortion must be operative even in the so-called "pure" crystals.

In the ideal crystallization of a solid solution, there are several conditions prescribing the points at which solute atoms must attach themselves to the solvent lattice. The frequency of their attachment—that is to say, the equilibrium relations between the atomic fractions present in the melt and in the crystal—is a matter of physical chemistry and is not germane to the present discussion. On the other hand, the arrangement or spatial disposal of the foreign atoms is a matter of highest importance. These must, under equilibrium conditions, assume such positions as not to degrade the symmetry of the parent lattice. Besides the theoretical grounds for this concept, there are numerous experimental checks, among which may be cited the fact that all the physical properties of a single phase of a solid-solution series are continuously varying and without abrupt changes in crystal class, optical effects, etc. Furthermore, since the presence of a foreign atomic species is attended by a lattice distortion, a consequence of the varying atomic volumes of solute and solvent atoms, the distortions must so distribute themselves as to minimize the tendency of the larger atoms to increase the lattice dimensions. In other words, the potential energy of the crystal must be a minimum, and to satisfy this requirement, the distortions, and hence the solute atoms producing

⁸ Walter Rosenhain: Solid Solutions. *Trans.* (1923) **69**, 1003–1034; see especially 1011–1017.

them, must be disposed in a well-nested or close-packed arrangement.⁹

Every solute atom will be surrounded by an aureole of distorted lattice structure (see Fig. 4), as has been brought out by Rosenhain. This primary distortion, being symmetrically distributed, is, of course, not detectable by optical means which, by their nature, give essentially statistical effects over enormous volumes of the structure. X-ray methods, however, give some evidence of lattice distortion. Davey,¹⁰ in making precision measurements of lattice constants, was struck by the especial sharpness of the diffraction lines of 99.9995 per cent. pure tungsten. The inference is that the pureness of the crystals allows atomic planes to approach true flatness and give an unspread X-ray reflection beam, while the presence of the usual impurities ordinarily gives rise to somewhat spread reflections by slightly curving the reflecting planes.

The lattice distortion must be greatest in the immediate vicinity of a solute atom and of rapidly decreasing magnitude at increasing distances from it, where the disturbing influence of the foreign particle is felt more and more remotely.

Mechanism of Plastic Deformation of a Crystal Containing a Single Solute-atom Species in Minute Amount

If the model of a crystal whose impurity consists of a single solute-atom species, as above presented, is examined, the possibility of its explaining many otherwise anomalous crystalline behaviors will become apparent. While the applicability of the theory is general, the lead

⁹ I have been very fortunate in being able to discuss this manuscript with Prof. J. T. Norton and Mr. B. E. Warren of the Department of Physics, and with Dr. R. H. Aborn and Mr. E. W. Brugmann of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology. In the opinions of these crystal-structure investigators, one of the chief objections to this hypothesis is that there is no experimental evidence for a regular arrangement rather than a random arrangement of solute atoms in a dilute solid solution and that, moreover, certain investigations (C. H. Johansson and J. O. Linde: Gitterstruktur und elektrisches Leitvermögen der Mischkristallreihen Au-Cu, Pd-Cu und Pt-Cu. *Ann. Physik* (1927) **82**, 449-478) point to a random solute atom disposal in unannealed metals. This objection certainly can not be disregarded in the evaluation or the modification of a final working hypothesis. The present paper is a purely speculative one, without essential experimental backing, and represents an attempt to explain hardening and slip-striae production assuming the *ideal conditions of equilibrium crystallization*. The assumption of equilibrium is essentially a simplification in the development of the hypothesis. In so far as actual conditions may be found to depart from the assumed ideal conditions, to just such a degree must the present hypothesis be modified to include such irregularities, should its general outlines meet with any favor.

¹⁰ Wheeler P. Davey: Precision Measurements of the Lattice Constants of Twelve Common Metals. *Phys. Rev.* [2] (1925) **25**, 758.

sulfide structure will be employed to demonstrate a few of its consequences. A view of this structure is shown in Fig. 1.

The symmetry of the lead sulfide structure demands an isometric distribution of distortion centers, and of the possible methods of grouping the solute atoms occasioning these distortions, the face-centered cubic arrangement offers the closest packing. Thus the atoms would have the arrangement shown in Fig. 3.

For the purposes of observing the effect of solute atoms on deformation it will be necessary to gain some picture of the manner in which the distortions disturb the planes along which translation occurs. Fig. 2, corresponding to the unit cell in Fig. 1, shows one family of translation

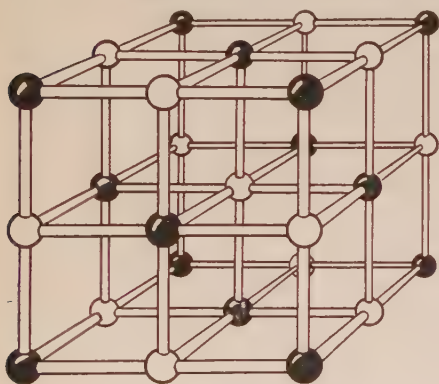


FIG. 1.

FIG. 1.—LEAD SULFIDE STRUCTURE.

After the method of representation employed by Hull. Black balls represent positive ions, white balls negative ions, or vice versa.

FIG. 2.—ONE SET OF ATOMIC TRANSLATION PLANES (001) CORRESPONDING WITH THE STRUCTURE SHOWN IN FIG. 1.

One translation direction of these planes (a direction of alignment of consecutively like-charged atoms) is indicated by the arrow. Note that cross-sections of the lattice on $(1\bar{1}0)$ planes intersect the translation planes along translation lines. Any distortions of these lines may thus be pictured on these cross-sections.

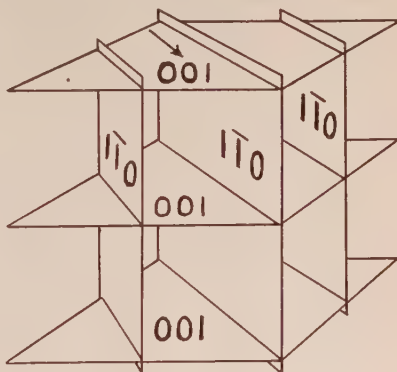


FIG. 2.

planes together with one of their two possible translation directions. It will be observed that by taking cross-sections of the lattice on $(1\bar{1}0)$ planes, which include the translation direction $[110]$, the influence of distortions on both translation lines and translation planes (001) may be studied. Fig. 3 shows the location of such cross-sections with reference to the lattice as a whole, and Fig. 4 gives a single detailed section taken on plane a , Fig. 3. Note that each of the solute atoms is surrounded by its aureole of distorted lattice.

As a graphical means of representing the varying magnitude of the distortions, plots are included at the left of Fig. 4. On these, the deviations of translation lines from straightness are plotted against the positions of the lines in the lattice cross-section. By plotting several of these

graphs, one for each cross-section between a and b , Fig. 3 (such as graphs c , d , e , f , etc., Fig. 4) and combining these, a composite graph is obtained which gives a measure of the deviation of each translation plane from flatness (Fig. 4h). It will be noted that the distortion of a plane is never absolute zero, and that the translation planes of least distortion occur halfway between the planes containing the disturbing solute atoms.

For translation to occur with least resistance, the planes between which the shearing occurs must be absolutely flat. Such a condition does

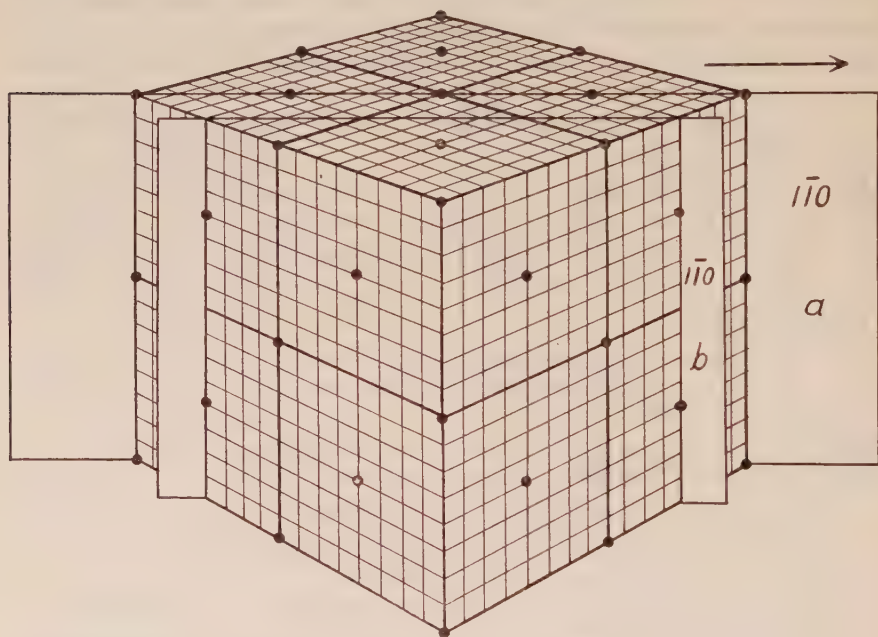


FIG. 3.—PORTION OF THE (IMPURE) LEAD SULFIDE LATTICE SHOWING THE LOCATION OF CROSS-SECTIONS ON 110 PLANES.

The small cubes are single unit cells of the lead sulfide structure, no attempt being made to represent solvent atoms. Black dots indicate the face-centered distribution of solute atoms of a single species in the lattice.

not obtain in any crystal containing the least trace of impurity, but it is reasonable to expect that, this ideal situation being absent, shear will be initiated upon application of sufficient stress, between sets of translation planes showing the least differential distortion, such as those in the regions of k , l , m , and n , Fig. 4, halfway between solute-atom planes. In the regions of the solute-atom planes, according to this, the crystalline structure is initially hard and rigid because of the locking action of the primary distortions.

As stress is applied to the crystal beyond the pure elastic limit of the weakest pairs of planes (near k , l , m , and n , Fig. 4) the restoring forces

of the ions in these planes are overcome and translation takes place. As it does so, the original, closely nested disposition of distortions (Fig. 5a) is altered and a new, less compact distribution approached (Fig. 5b). Since, by hypothesis, the original distortion distribution was that of least potential energy, it is obvious that the potential energy of the lattice must be increased by translation, the distortion aureoles tending to assume positions nearer one another, where, not nesting so compactly, they expand the lattice. The force necessary to continue translation thus consists not only of that necessary to overcome interatomic friction, but also of that necessary to increase the dimensions of the crystal.

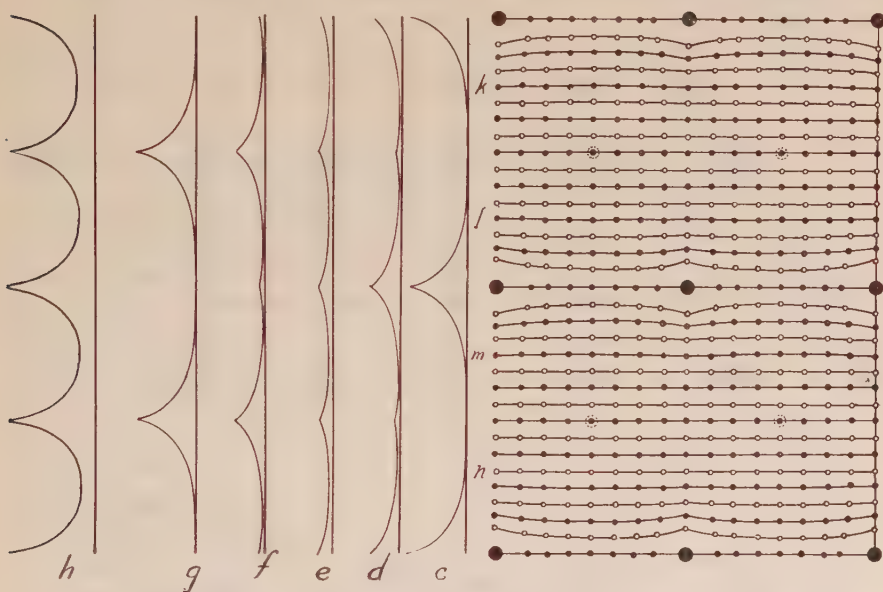


FIG. 4.—DETAILED SECTION OF LATTICE ALONG PLANE *a*, FIG. 3, SHOWING DISTORTIONS OCCASIONED BY SOLUTE ATOMS.

Curve *c* shows graphically the deviation of a translation line from straightness as a function of its position in the cross-section; *g* is a similar curve for plane *b*, Fig. 3. In this case the solute atoms occupy the dotted positions shown in the above figure. Similarly, *d*, *e*, and *f* are distortion curves for cross-sections intermediate between *a* and *b*, Fig. 3. Curve *h* is a composite of *c*, *d*, *e*, *f*, and *g*, and may be taken to represent, roughly, the deviation of a translation plane from flatness, as a function of its lattice position.

In other words, the planes must not only be slipped apart during deformation but they must also be lifted away from one another. A partial confirmation of this is seen in Beilby's¹¹ findings that the specific gravities of crystals decrease on cold working, although this investigator sought thereby to add probability to the amorphous-metal hypothesis.

¹¹ G. T. Beilby: The Hard and Soft States in Metals. *Jnl. Inst. of Metals* (1911) 6, 18.

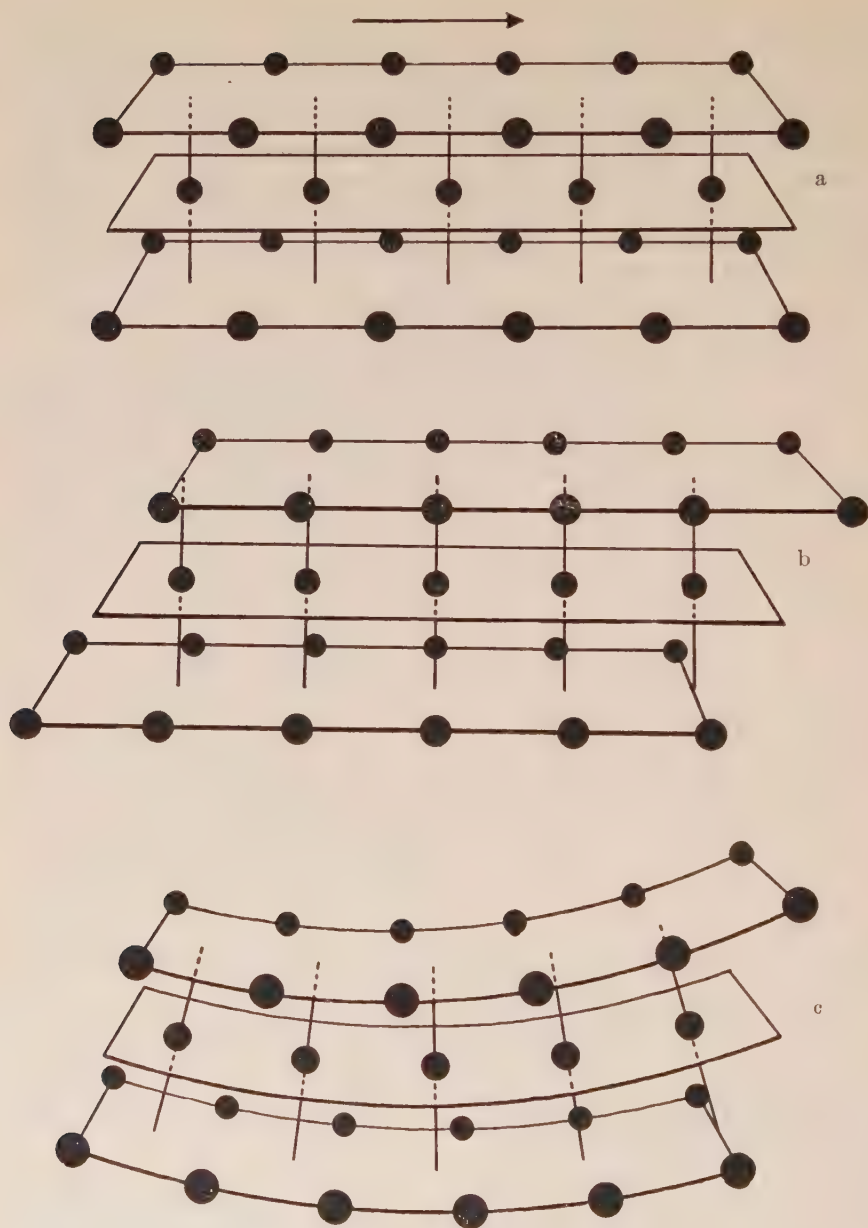


FIG. 5.—(FOR CAPTION SEE PAGE 383.)

It is important to note that, since the distortions become increasingly great in the neighborhood of the solute atoms producing them, the "hills" up which the planes are pushed become continually steeper. Thus, the pair of planes initiating translation will probably continue for a distance of several atom diameters without any appreciable increment of force necessary to continue the movement, but a point is eventually reached where less force is required to start translation anew along the planes of next least differential distortion than to continue it on the initial pair. New planes thus operate as translation planes as their predecessors are blocked.

This process continues until the lattice is in an almost unstable condition; that is, until further translation on any pair of planes would so far separate them that cohesion under the load used would no longer be possible. Further increase in stress then produces cleavage.

Complications Due to the Presence of More than One Solute-atom Species

The simple case outlined above is only a start in the direction of explaining actual lattice deformations, which may become quite complicated with the presence of more than one solute-atom species. The writer hesitates to discuss the more complex general case because of lack of knowledge of the laws governing the distribution of solute atoms when several species are present. Yet it may not be amiss to set down a few preliminary remarks on certain aspects of the problem, bearing in mind, however, the speculative nature of the discussion.

Whatever complex grouping the various solute atoms might conceivably assume, it is essential that they preserve the lattice symmetry. There appear to be two manners in which this may be accomplished:

(1) The solute atoms of all species might arrange themselves throughout the lattice in complex, heterogeneous groups, each group maintaining the symmetry of the structure or a higher symmetry.

FIG. 5.—DIAGRAMMATIC REPRESENTATION OF INCREASE IN POTENTIAL ENERGY AS A RESULT OF THE REDISTRIBUTION OF DISTORTION CENTERS (BLACK DOTS) ACCOMPANYING TRANSLATION.

The figures show three strips of (001) planes containing solute atoms. The translation direction is indicated by the arrow. No attempt is made to show the solvent planes.

a. Original face-centered cubic arrangement of distortion centers. Note that each black dot in the central plane nests equidistant from four others in the upper and four in the lower plane (besides four in the same plane, only two of which can be seen in the figure). This is the arrangement of closest nesting of distortions and consequently of least potential energy of the lattice.

b. Distribution of distortion centers approached when the planes undergo translation. Note that now each distortion center in the middle plane rests between only two others in the upper plane and two in the lower plane (besides those in the same plane). This nesting is less compact and hence the lattice must expand to accommodate the new packing of distortions.

c. Possible explanation of bending during deformation. Part of the distortions (right side of figure) behave as in b, while others (at left), in response to demands of less potential energy, either fall back into the original position or remain there from the start. The result is a warping or curling of the planes—*Biegegleitung*.

(2) Each species of solute atom might distribute itself throughout the lattice in close-packed arrangement without essential regard to the presence of other species, each species behaving as if it were the only one in solution in the pure lattice (see Fig. 6).

Since chemical analyses show that impurities may be present, within their limits of solubility, in any varying relative amounts whatever, it appears that possibility (1) can not obtain. A continuously variable arrangement is demanded by the nature of solid solutions, and it is obvious

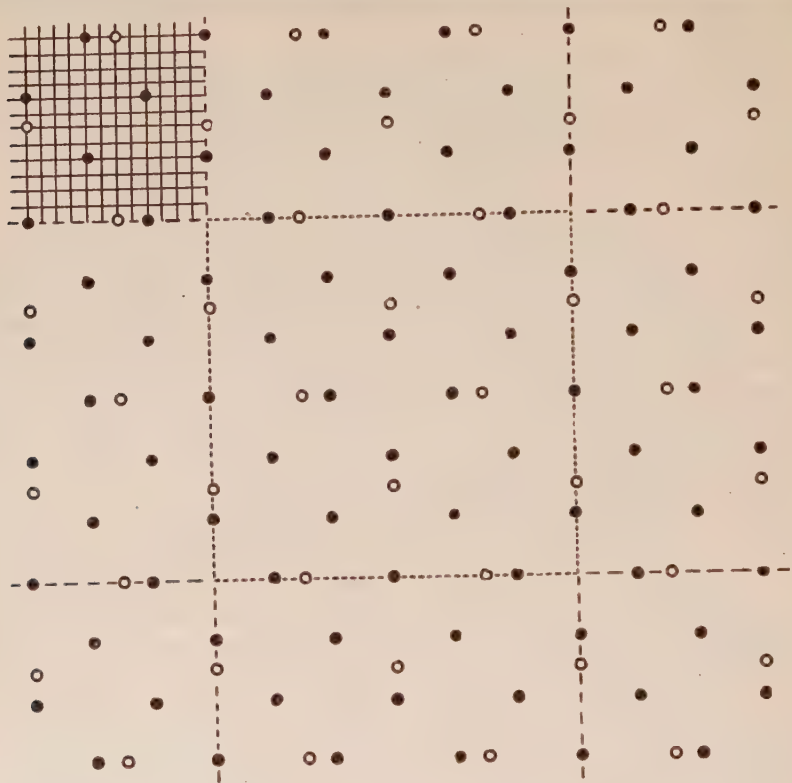


FIG. 6.—A CONCEIVABLY POSSIBLE DISPOSAL OF SOLUTE ATOMS IN THE LEAD SULFIDE LATTICE WHEN TWO FOREIGN SPECIES ARE PRESENT.

The figure is a (001) plane of the lead sulfide structure on which both foreign species are in phase. The solvent atoms are not shown, but the size of the lead sulfide unit cells is indicated in the upper left corner of the figure. Each species of solute atom is disposed in face-centered arrangement without regard to the presence of the other species. The dotted lines delimit the solid-solution unit cells, in the center of which all solute-atom arrangements are in phase.

that (1) requires a new complex grouping for any slight concentration change affecting a single constituent—a requirement which would necessitate discontinuous physical properties. It is difficult to escape the conclusion that while (2) apparently defeats the fullest requirements of close packing, it is the more plausible possibility.

Assuming disposal (2) to obtain, several crystallographic consequences at once follow. It is customary to designate as the unit cell of a crystal the smallest portion of the atomic structure which, by simple translation along its coordinates, will reproduce the entire lattice, and which, therefore, has the symmetry of the lattice as a whole. If arrangement (2) is a true picture of actual conditions, it is manifest that, strictly speaking, the unit cell must include that volume of the lattice contained between the nearest planes along which all impurity arrangements are 180° out of phase with one another, the center of the cell marking the position where all arrangements are in phase (see Fig. 6). Thus the unit cell would be larger:

(a) The smaller the concentrations of the solute atoms, since small concentrations require the unit arrangement of each species to be of great dimensions.

(b) The smaller the concentration differences between the various solute-atom species, excepting exact equality, since nearness of concentration values enhances the distances between "in phase" planes.

(c) The greater the number of solute-atom species, since this would make the "in phase" relations more infrequently satisfied simultaneously.

The enormous size of a dilute, complex, solid-solution unit cell may be of only academic interest for most purposes, but it has, if true, a very real significance in deformation phenomena. The exceedingly low frequency of major distortion periods would account for the fact that slip striae are visible with the eye, alone or aided by low magnifications.

The effect of all solute atoms on translation behavior may be studied by the method previously employed. Thus, by plotting a curve representing the distortion occasioned by each foreign species present in the lattice and combining these to form a single composite curve, the total lattice distortion may be represented. In general, such a graph will have numerous maxima and minima of various relative magnitudes. Planes in the regions of least minima initiate translation (Fig. 7) and a sequence of events essentially similar to that previously discussed ensues.

The topography of the external surface of an originally smooth crystal will bear a close relation to its distortion curve after deformation, as shown in Fig. 7, the slip striations corresponding with positions of strong minima on the curve. The detailed character of the striations may conceivably vary widely. If the minima are sharp—*i. e.*, the curve is steep in these regions—the resulting crystal surface may be cleanly serrated and the whole crystal appear to be constituted of discrete "slip blocks," as shown in Fig. 8A and B. On the other hand, if the minima do not differ greatly in magnitude from the maxima, and the curve has a generally slight slope in the minimum regions, the deformed crystal may present the appearance of a necked cylinder, the surface being undulating, as shown

in Fig. 8C and D.¹² This would account for the absence of marked serrations noted by Hoyt.¹³

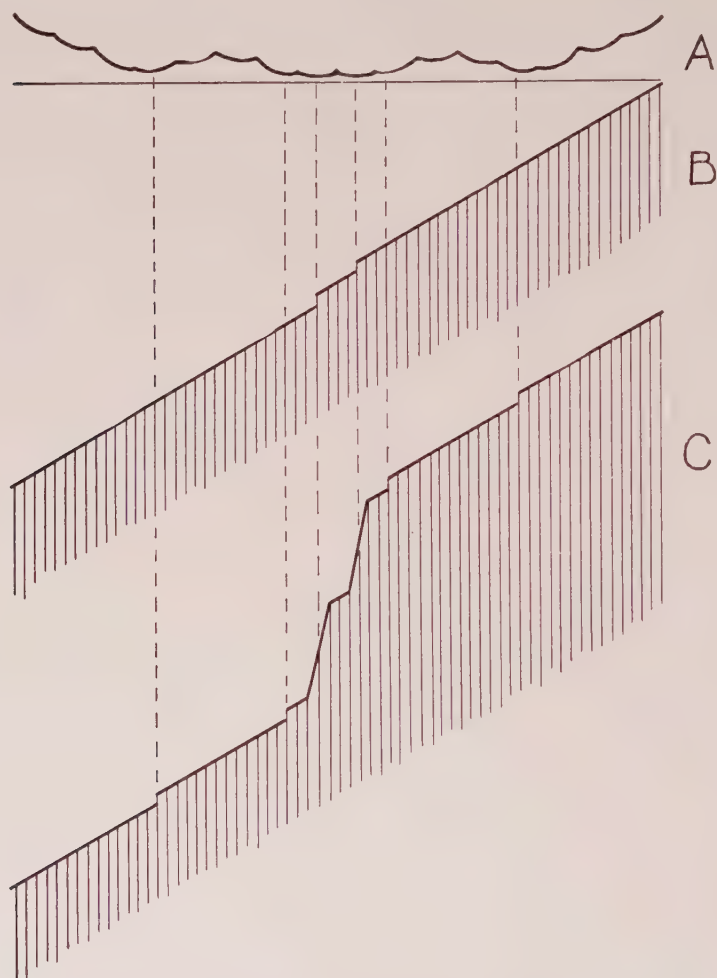


FIG. 7.—RELATION BETWEEN THE TOPOGRAPHY OF THE SURFACE OF A DEFORMED CRYSTAL AND ITS TRANSLATION-PLANE DISTORTION CURVE.

A shows the distortion curve of the crystal; B and C, cross-sections of the crystal normal to its surface. In B, deformation has just started along the two planes of minimum initial distortion. In C, several other planes have also slipped in regions of somewhat greater distortion.

It is interesting to note that the mechanism described might account for the curved spots encountered on Laue diagrams of deformed crystals.

¹² Compare with the photograph given by M. Polanyi and E. Schmidt: *Verfestigung und Entfestigung von Sn Kristallen. Zeitschr. für Phys.* (1925) **32**, 700, Fig. 12.

¹³ *Op. cit.*, 124-125.

The bunching of distortion centers obviously places the crystal in an unstable equilibrium, and the tendency of the lattice to seek a lower level of potential energy might possibly cause a lattice curvature somewhat as

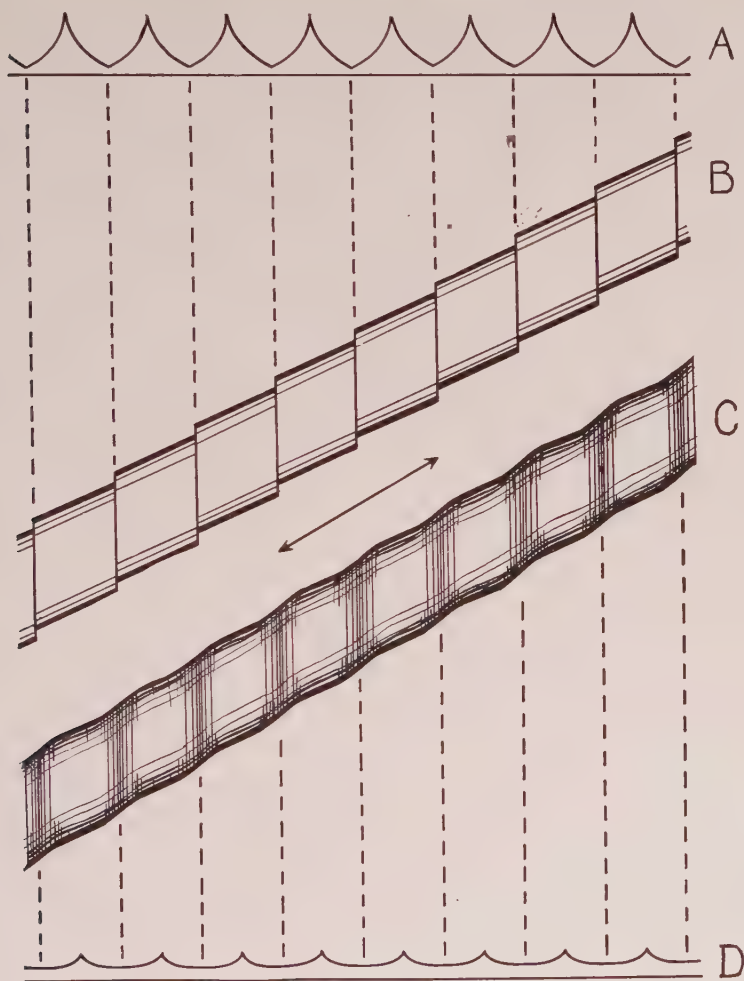


FIG. 8.—INFLUENCE OF THE SHARPNESS OF DISTORTION-CURVE MINIMA ON THE TOPOGRAPHY OF THE DEFORMED CRYSTAL.

B and C, originally single-crystal wires, have distortion curves A and D, respectively. In A, the minima are sharp; in D broad and ill-defined.

B thus deforms by block slipping since the regions of weakness are highly localized. C deforms by a distributed slip since its regions of weakness are broad; it thus presents the appearance of a necked cylinder, constriction taking place over broad areas.

indicated by Fig. 5c. It is also of interest to observe that the distributed, differential translation described degrades the symmetry of the crystal by redistributing the solute atoms in the lattice. Since the optical proper-

ties are dependent on the lattice symmetry, an originally isometric crystal should be expected to display anisotropism as a result of translation. Confirmation of this is found in Veit's experiments on fluorite,¹⁴ which, normally isotropic, became birefringent in the regions of the translation striae accompanying deformation. It is recognized, of course, that this effect may also be explained by simple strain or bending.

There are several other consequences of this hypothesis which are well in accord with experimental data, among which might be mentioned the decreased electrical conductivity of crystals due to impurities, the parallelism of electrical resistance and hardness curves in solid-solution series, the temperature rate of increase of ductility, and the necessity of secondary twinning in the deformation of concentrated solid-solution crystals.¹⁵ However, these topics are beyond the scope of the present brief paper.

While the details of the foregoing discussion may be in error, it seems that some such conditions may account for strain-hardening. Of course, it has been assumed, for the sake of simplicity, that the crystalline structure forms under the ideal conditions of equilibrium, conditions which perhaps are only very closely approached in nature. In actual crystallization the solute atoms possibly do not have sufficient time to assume a precisely accurate close-packed arrangement, but certainly they must approach this condition approximately in an attempt to keep the potential energy of the crystal a minimum. Admitting this, it follows that, by translation, this condition of (at least approximately) least potential energy must be destroyed if impurities are present, and the stress necessary to accomplish this beyond elasticity accounts qualitatively for strengthening.

DISCUSSION

J. W. GRUNER, Minneapolis, Minn. (written discussion).—Dr. Buerger's hypothesis might be accepted by many students of crystal structure but for one major objection: he considers all crystals as solid solutions on account of the impurities in them. These impurities under ideal conditions are supposed to form a geometrical lattice similar to the lattice of the solvent.

Let us assume, for example, a metal with a purity of 99.9 per cent. The remaining 0.1 per cent. could be all one element, but more likely it would consist of a number of different elements. If it were one element, the unit cell of its lattice would necessarily be of such dimensions that like atoms would be 10 times as far apart in the solute as like atoms of the solvent in corresponding directions. It is difficult to see how the solute atoms could have this orienting power with respect to one another over relatively great distances, probably over distances greater than assumed in this ideal case. Since the solute atoms would have to occupy geometrically equivalent positions with

¹⁴ Kurt Veit: Künstliche Schiebungen und Translationen in Mineralien. *Neues Jahrb. f. Min. Geol. u. Pal.* (1922) Bl. Bd., 124.

¹⁵ M. J. Buerger: The Plastic Deformation of Ore Minerals. *Am. Mineral.* (1928) 13, 49.

respect to those of the solvent atoms (as shown in Fig. 4), it is obvious that the solute atoms could not be present in any random proportion without violating the geometrical symmetry underlying the theory of space groups. It was this consideration that led Tammann to his hypothesis of "reaction limits" which, however, was not accepted by most investigators.

The arrangement presented in Fig. 6 is a case where solute atoms evidently occupy positions not equivalent to those occupied by the solvent atoms (not shown in the figure). The symmetry of the outlined new unit cell for the solute atoms is lower than that of a theoretical lead sulfide structure. This would probably be the case in most solid solutions, if the outlined hypothesis is correct. Under the most favorable conditions and by precision measurement in X-ray analysis, it may become possible in the future to detect such lowered symmetry.

Grain Growth in Metals Caused by Diffusion

BY FLOYD C. KELLEY,* SCHENECTADY, N. Y.

(New York Meeting, February, 1928)

THE literature of the last decade is rich with information relating to the cause and means of control of grain growth in pure metals, but is deficient concerning the role diffusion plays in grain growth, although during this period many new products that depend on diffusion for their properties and success have been developed. Among these are cementation products, produced by calorizing, chromizing, and carbonizing, or by mixing, pressing, and sintering powdered metals such as Syke's iron-molybdenum die material, Genelite, and Elcon Metal (copper, tungsten) etc.

This is a fertile field for new developments, but before it can be utilized to the fullest extent there must be a thorough investigation of the processes by which diffusion and grain growth take place. Grain growth plays no small part in the process and certainly the physical properties of these products depend largely on the grain size and state of equilibrium produced. The field of investigation does not end here, but may be extended to the effect of diffusion on impurities, segregations and dendrites in the broad field of ferrous and non-ferrous metallurgy.

A number of years ago the author investigated several of these cases and noted, with striking regularity, the pronounced effect of diffusion in promoting recrystallization and grain growth. An example of this phenomenon is given in his paper on chromizing¹ which contained photomicrographs of large radial or columnar crystals produced by diffusion of chromium in the solid state. Another manifestation of this effect was discussed by Austen,² who showed the part hydrogen plays in the decarburization of steel and the effect of diffusion upon the grain structure.

DIFFUSION OF METALS IN IRON

It seems to be a general law, whenever two metals are brought into intimate contact at a temperature at which diffusion takes place, that a comparatively rapid, or abnormal, grain growth results. The grains

* Research Laboratory, General Electric Co.

¹ Floyd C. Kelley: Chromizing. *Trans. Am. Electro-Chem. Soc.* (1923) **43**, 351.

² Charles R. Austin: Hydrogen Decarburisation of Carbon Steels with Considerations of Related Phenomena. *Jnl. Iron and Steel Inst.* (1922) **105**, 108.

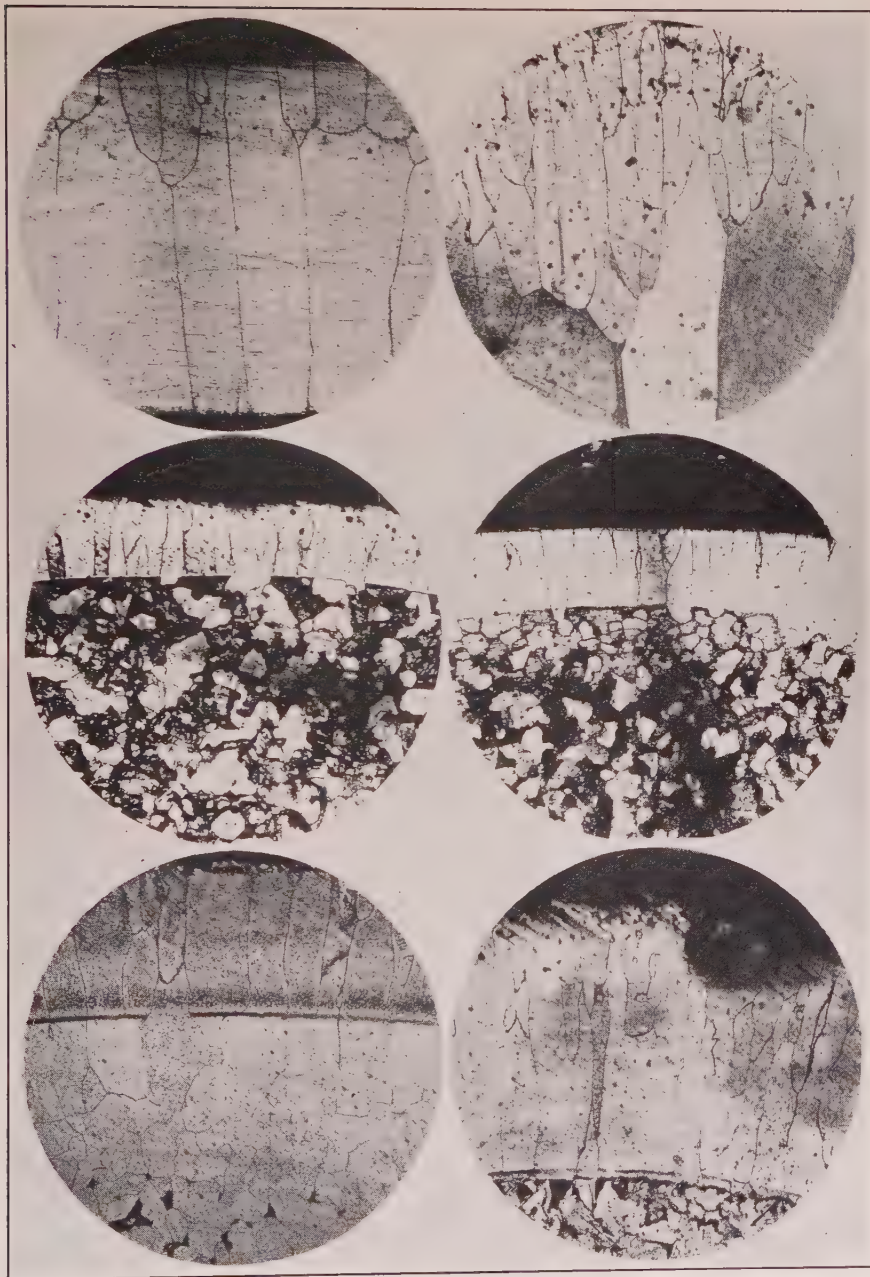


FIG. 1.—COLD-ROLLED IRON CHROMIZED AT 1300° TO 1350° C. FOR 4 HR. $\times 70$.
 FIG. 2.—COLD-ROLLED IRON CHROMIZED AT 1300° TO 1350° C. FOR 8 HR. $\times 42$.
 FIG. 3.—COLD-ROLLED IRON FIRED IN $\text{Si} + \text{Al}_2\text{O}_3$ AT 1100° C. FOR $3\frac{1}{2}$ HR. $\times 40$.
 FIG. 4.—COLD-ROLLED IRON FIRED IN $\text{Sn} + \text{Al}_2\text{O}_3$ AT 1100° C. FOR $3\frac{1}{2}$ HR. $\times 40$.
 FIG. 5.—COLD-ROLLED IRON FIRED IN PURE Mo POWDER AT 1350° C. FOR 3 HR. $\times 90$.
 FIG. 6.—COLD-ROLLED IRON CALORIZED AT 1000° C. FOR 4 HR. AND REHEATED TO 1300° C. FOR 3. HR. $\times 60$.

(Reduced to 65 per cent. original scale, original magnifications given.)

are nearly always oriented with their long axes parallel to the direction of diffusion. This is shown in Figs. 1 and 2, which are typical of radial or columnar structure produced by diffusion of chromium in iron.

There is evidence that when the supply of chromium at the surface of the iron is limited, diffusion beyond a certain point results in grain refinement of the surface grains, and a loss of the sharp line of penetration. This is shown by a comparison of Figs. 1 and 2. The sample in Fig. 2 was heated twice as long as that in Fig. 1. The chromium for diffusion was furnished by a mixture of 55 per cent. Cr and 45 per cent. Al_2O_3 in actual contact with the surface.

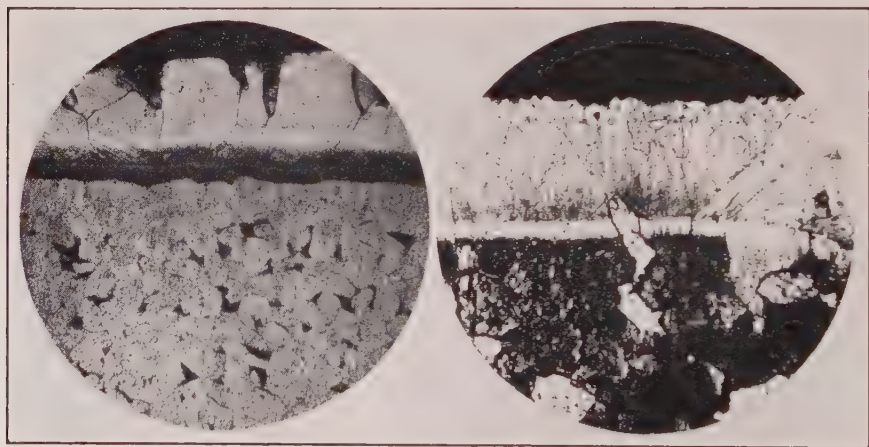


FIG. 7.—COLD-ROLLED IRON FIRED AT 1250°C . FOR 3 HR. IN $\text{Mn} + \text{Al}_2\text{O}_3$. $\times 100$.

FIG. 8.—COLD-ROLLED IRON FIRED IN CHROMIUM AT 1300° TO 1350°C . FOR 4 HR. $\times 70$.

(Reduced to 65 per cent. original scale, original magnifications given.)

Many other metals diffuse into iron in the same way, as is shown in Figs. 3 to 7. The resemblance between the crystal structures of the diffusion areas is very striking, with the exception of the sample shown in Fig. 7. The diffusion of manganese in iron is very slow even at the melting point of manganese, and from the color of the surface crystals under the microscope one can tell that they are very rich in the diffusing element.

METHOD OF GRAIN GROWTH

The question as to the manner in which grain growth takes place, the effect of diffusion on orientation, and grain size are all of importance to the future development of this field and metallurgy in general.

The diffusing metals in all of these experiments were not over 200 mesh mixed with precipitated Al_2O_3 with the exception of the one in which molybdenum was used, Fig. 5. Pure molybdenum metal was used in

this case. It would seem from these experiments where the vapor pressures of the diffusing elements are very low at the temperatures used, with the exception of aluminum, that diffusion took place almost entirely from particles in contact with the surface of the iron. Outward diffusion of the iron was limited by the Al_2O_3 to those particles in contact with the iron surface, which is a very short distance compared to the length of the columnar grains. Diffusion under these conditions is in the direction of the center of the sample. The surface grains of iron absorb the particles of powdered material, and the direction of diffusion of the material determines the direction and position of the long axes of the grains. Grain growth starts by a surface grain of iron absorbing the powdered material and the grains thus started continue to grow inwards by absorption of smaller grains through migration of the grain boundaries. The grains of iron absorbed by the continually growing mixed crystal are forced to change their orientation to conform with that of the absorbing grain.

Close examination of the sample treated in pure powdered molybdenum, Fig. 5, where diffusion is allowed to take its course in both directions, shows that each columnar grain has grown upon the surface of a grain in the iron. This case shows that the iron grain has been the seed for grain growth and has probably forced its atomic arrangement upon the molybdenum-rich constituent as the iron diffuses out through it, unless the force of diffusion is sufficient to change its orientation.

FORCE OF DIFFUSION

"Force of diffusion" is a new term, and its introduction calls for some comment. While the author does not want to be dogmatic, it has seemed to him that the common laws of crystallization do not completely account for the observations he has made. The passage of a group of atoms through a metal lattice appears to exert a powerful force on the lattice, sufficient to produce reorientation, and this force is termed the "force of diffusion."

It may be that the dark line between seed grain and its continuation in the columnar represents a distortion of the crystal lattice. This distorted area would be due to the influence of diffusion and would act as a zone of transition between the different orientations of this grain with respect to the axis of diffusion.

There is a single large grain at the left of the center in Fig. 5, which extends across the boundary line between the iron grains of the core and the columnar grains at the surface. It shows no dark line across it. This particular grain by chance had the correct orientation for diffusion to take place with the greatest ease. There is no distortion of the grain through the influence of diffusion in this case and the dark line is lacking.

DIFFERENT FORMS OF GRAIN GROWTH

In Figs. 3 and 4 may be seen the results obtained by firing cold-rolled iron samples in silicon and tin respectively. The metal powders used for diffusion in these cases were mixed with Al_2O_3 , so diffusion took place in one direction only. There is diffusion of iron also, but not beyond the old surface. The number of columnar grains that seem to be joined to iron grains on the opposite side of the sharp line marking the distortion area are far fewer in both cases than in the one where pure molybdenum was used. Grain growth started at the surface of the samples by small grains of iron absorbing the diffusing material and extended by migration of the grain boundaries in the direction of the diffusing force. It seems as though the outward force of diffusion in the molybdenum-iron experiment had something to do with the positive linkage of the grains on opposite sides of the line of distortion.

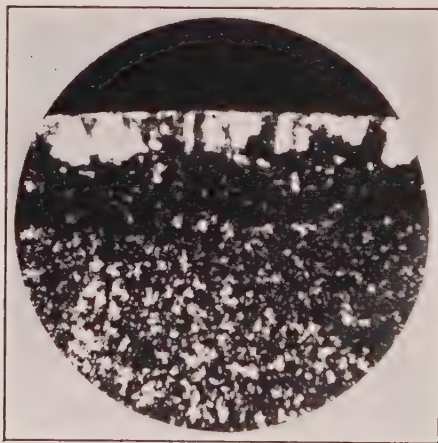


FIG. 9.—DRILL ROD DECARBONIZED IN HYDROGEN AT 850°C . FOR 4 HR. $\times 40$.
(Reduced to 65 per cent. original scale, original magnification given.)

Fig. 8 shows an abnormal case of diffusion of chromium in iron where the grains are not radial. There are two distinct bands or chromized layers; at about the center of the photograph is a single grain extending from the outer band across the inner band into the iron core. The grain shows no signs of this banded structure.

Experiments with iron and nickel at 1350°C ., where the nickel is in powder form, shows that the iron does not take up the nickel. If the sample of iron is packed in pure nickel powder and fired at the same temperature, the iron sample grows smaller and loses in weight, showing that diffusion takes place from iron to nickel.

The effect of decarbonization of iron by hydrogen is well known. Fig. 9 shows the radial grains produced on the surface of a sample of drill rod decarbonized in hydrogen at 850°C . for 4 hours.

RECENT WORK IN GERMANY

A paper by G. Grube,³ just published, deals with the diffusion of Cr, Al, W, Mo and Si into iron and Cr into Ni. It also gives the diffusion curves of Al, Cr, W and Mo in Fe. Electrolytic iron was used for the experiments. The mathematical determination of the coefficient of diffusion is discussed and also the resistance to corrosion of the various coatings obtained by diffusion. Grube brings out the following points:

1. It can be assumed that metals that crystallize in the cubic system will generally diffuse into iron.

2. Aluminum does not diffuse into iron below 640° C. even after heating for several days.

3. Radial crystals are grown on the crystal faces of the core.

4. The dark line of demarcation separating radial crystals and the core is not the limit of penetration of the diffusing material.

5. Diffusion takes place by an exchange of atoms between the diffusing metals. That is, for every atom of tungsten diffusing into iron an atom of iron diffuses into tungsten.

6. Diffusion through the radial crystals is at a maximum rate and in the direction of their long axes.

This work checks in a general way all of the findings described in this paper. Grube shows a photograph (Fig. 17) of the diffusion of molybdenum into iron which agrees exactly with the findings shown in Fig. 5 of this paper. The two experiments were conducted in the same way and bring out point 3 mentioned above.

He established point 4 by turning off the penetrated layer in a series of cuts. Each cut was only a fraction of a millimeter, and the material from each cut was analyzed. The percentage of diffusing element found was plotted against the penetration to give the diffusion curve. His curve for Al, Fe shows that the zone of diffusion from 6 per cent. to 0 per cent. lies in the core inside of the dark line of demarcation.

The reason for sharp falling off in the rate of diffusion at a penetration corresponding to the dark line might be accounted for by the consumption of an enormous amount of energy required to transfer an atom through the distorted area from one orientation to another.

Grube claims that the dark line of demarcation is produced by a difference in hardness of the core and the radial crystals at this point. He claims that it shows up on polishing and produces a low spot, which shows up as a shadow.

Grube's conception of the cause of the dark line does not agree with the author's and does not account for the absence of the dark line on occasional single grains which extend from the mixed crystal area into

³ Die Oberflächenveredlung von Metallen durch Diffusion. *Zeitschr. für Metallkunde* (1927) 19, II, 438.

the core of iron. Fig. 14 of his article shows one such grain in the lower right side.

He also showed that by packing a rod of electrolytic iron in tungsten powder and firing for 48 hr. at 1330° C. he obtained, by analyses of the rod and the tungsten powder, 0.4064 g. of W from the iron and 0.1400 g. of Fe from the tungsten powder, proving his point that diffusion takes place by exchange of atoms.

The second point of his paper referred to above is an extremely hard thing to prove by microscopic examination or chemical analysis. Pieces of iron calorized at these low temperatures, 640° C., show a physical change brought out on heating at low temperatures. They certainly do not take up much aluminum, but resist oxidation to heat much better than a blank piece of iron fired at the same temperature.

Grube's paper is a start in the right direction and he is to be encouraged to do more work along the same line. The orientation of the grains on either side of the dark line might be determined by X-ray analysis of a thin section. This would give some real information of value and help to explain just what occurs at the boundary between the columnar grain and grain of the iron core.

There are many other things which are out of the ordinary in this field of investigation which may be the subject of a future paper. The object of this paper has been to create an interest that will lead to such further investigation by others.

ACKNOWLEDGMENT

The author desires to acknowledge his indebtedness to Dr. S. L. Hoyt for his helpful suggestions and criticisms in the preparation of this paper.

DISCUSSION

T. S. FULLER, Schenectady, N. Y. (written discussion).—Mr. Kelley's observations on the change in size and shape of the peripheral grains of iron produced by diffusion are in accord with those of other experimenters.

Stead,⁴ in 1898, remarked that the decarburization of steel by heating in lime at 700° to 800° C. for several hours had a marked effect on the size and shape of the ferrite grains. Under this treatment they exhibited a columnar formation.

Austin,⁵ in 1922, observed a columnarisation of ferrite grains accompanying decarburization in hydrogen. He said "The hypereutectoid steel showed the phenomenon at all temperatures, though it is true that at 1000° C. the columnarization is only slight and confined to the edge of the bar; but at 850° C. it is clearly indicated, while at 680° C. the continued decarburization for three or four days resulted in the

⁴ J. E. Stead: *The Crystalline Structure of Iron and Steel*. Iron and Steel Inst. (1898) **53**, 145.

⁵ C. R. Austin: *Op. cit.*, 93.

formation being very pronounced." Austin further investigated the effect of hydrogen molecule on hypoeutectoid and hypereutectoid steels, and remarked, "Both were conducted under practically identical conditions at 680°C ., and gave similar practical results, with the exception of the difference in the form of the crystal growth taking place in the decarburized areas; the high-carbon sample presented a columnar structure, the low-carbon a perfectly equiaxed one."

Again, in an effort to determine whether hydrogen molecules alone were capable of producing columnarisation, Austin heated "small cylinders of Armco iron containing about 0.02 per cent. carbon in a moist atmosphere of hydrogen at 680°C . for 12, 24, and 48 hr. respectively. On comparing the microstructure of these with that of a portion of the untreated iron, the only difference to be observed was perhaps a slight coarsening of the grains which maintained their equiaxed polygonal form



FIG. 10.— $\times 100$.

throughout. It would therefore seem that the production of elongated grains is at least not directly due merely to the disturbing influence of the molecules of hydrogen gas when diffusing into, or effusing from, the heated metal."

The photomicrograph (Fig. 10), taken in the writer's laboratory, shows the effect of heating drill rod in an atmosphere of hydrogen, at a temperature of 1000°C . for 8 hr. A columnar structure of the peripheral grains not unlike that produced in Mr. Kelley's samples by chromium, silicon, tin, etc., is evidenced. Such columnarisation, it seems reasonable to suppose, has been produced in the drill rod by the migration of carbon atoms toward the periphery.

J. ALEXANDER, New York, N. Y.—I am very much pleased to see metallurgists awakening to the fact that the principles of physical chemistry are of vital importance in what occurs in the heat treatment of metals.

One of the first references to diffusion in metals that I recall is the experiment of Roberts-Austen, who laid a block of lead on top of a block of gold and after five years found, by analyzing the lower layer of the lead and the upper layer of the

gold, that the lead had diffused into the gold and the gold had diffused into the lead. These slow motions of metals happen at room temperature in many other cases. Tin and lead will anneal at room temperature.

One point I would like to ask about is the influence of the amount of intercrystalline material, and whether a large part of the diffusion might not occur in the intercrystalline material instead of directly through what seems to be a homogeneous crystal. The reason I ask the question is this: If you cast a solution of gelatin into two cups, and cool one quickly and the other slowly, the rate of diffusion in the respective jellies of ordinary crystalloids will be quite different; but on standing, since gelatin also anneals at room temperature, the quickly cooled one later on comes up to the same crystalloid diffusion speed as the slowly cooled one. So that the internal structure, apart from the chemical composition, seems to be an important factor in diffusion.

Another process, which apparently goes on when you heat-treat a metal, is what is commonly called the Ostwald ripening, the general tendency being for small particles to be absorbed by large ones; that is, larger particles tend to grow at the expense of small ones, and I wonder to what extent that phenomenon is evident.

This diffusion ring might conceivably be an instance of the rhythmic diffusion rings known under the name of Liesegang's rings. It is possible that this might be a factor to be considered and I wonder to what extent the phenomena which are known in physical chemistry under the name of rhythmic diffusion occur in metals. Not having experimented with the metals directly, I cannot say, and I simply put that as a question.

L. W. MCKEEHAN, New Haven, Conn.—This paper is probably worth considering in connection with the other methods of developing crystals which are well known and all of which involve some gradient—a gradient in temperature, a gradient in strain, or something of that kind. Here I think a gradient in composition, in concentration of the diffusing element, makes the stability of the crystal structure at a given point diminish until it becomes impossible to maintain the old arrangement and a new arrangement is forced upon it. The arrangement which has been supplied by the diffusion up to that point is simply continued and added to, and the growing crystal continues into the material, just as the growing crystals in an electrolytic deposit continue as we add atoms from the electrolyte to the arrangement of the crystals already formed.

S. L. HORT, Schenectady, N. Y.—I believe that the field covered by Mr. Kelley's paper is really quite broad in metallurgy. For example, in 1922 I observed that a bronze alloy containing about 5 per cent. tin, whether chill cast or slowly cooled in the furnace, would decrease considerably in grain size on being annealed at around 850° C. That was just before I became aware of the work which Mr. Kelley had already done in the field and it seemed to be logical at that time to conclude that this change in grain size must have been due to, and certainly was accompanied by, the diffusion of the tin and the copper, and that we were dealing with a phenomenon which had received almost no attention in the literature. If it is true—and I certainly think Mr. Kelley demonstrates that it is true—that recrystallization is produced when metals diffuse into each other, we may expect that to be active in various other branches of metallurgy. For instance, the granulation which occurs in steel seems to me to be more readily accounted for on this basis than on any other with which I am familiar. We know that the dendrites in steel are not homogeneous and that at the temperature over which granulation is said to occur, diffusion of the phosphorus, oxygen, carbon, and so forth, can take place readily, and therefore it would seem logical to associate granulation with the diffusion which takes place

at that point, and by the same token we probably would associate ghost-lines and things of that character with diffusion which takes place. Possibly the grain refinement produced in steel simply by annealing has a direct relation to the diffusion which takes place.

It would seem to me to be very well for metallurgists to keep this work in mind—it certainly is of fundamental importance—and see if we do not have in this work, which is described for the first time by Mr. Kelley, an explanation of many of the phenomena which at present interest us, in passing, but which we set aside for some future day for satisfactory explanation.

Z. JEFFRIES, Cleveland, Ohio.—I might call attention to a few things in connection with this paper for suggestive purposes. The first is that most of the samples were steel or iron samples treated above the critical temperature, and a good many of the diffusing elements are elements which destroy the gamma phase. In a sample like that shown in Fig. 3, it might be assumed that the case produced at a temperature of 1100° C. contained enough silicon to destroy the gamma space lattice of the iron completely in the outer regions. Then on cooling to room temperature, the outer case would not undergo an allotropic transformation but the inner portion would. That may have some bearing on the line between the case and what might be called the core.

It is not out of the question, however, that there is in some cases what might be called a shrinking membrane which moves with the main body of the material which is being treated, or the solvent material. Those moving membranes are common in chemistry in the field of osmosis, where the containing membrane may either gain or lose total number of atoms, and if the containing membrane gains atoms it swells and if it loses atoms it shrinks in proportion. It seems not out of the question that there may be some sort of a membrane, composed possibly of some non-metallic material in part, through which the atoms of iron on the one hand can diffuse toward the case and through which the atoms in the case may diffuse to get into the iron or other solvent material.

Finally I should like to second Mr. McKeehan's remarks about the concentration gradients which are known to be very important in directing and controlling grain growth.

There is one further factor which might be considered and that is obstruction gradients, a type of grain-growth control which has been referred to before in the literature on grain growth and which would obtain in the case of Fig. 9, the drill rod.

P. A. E. ARMSTRONG, New York, N. Y.—Mr. Kelley's paper is almost entirely directed to grain-growth phenomena in metals caused by diffusion of one metallic element in another, and my remarks only deal in part with the subject matter of his paper.

To me the columnar structure portrayed in the various photomicrographs is clearly alpha iron, or what the later day metallurgists describe as "delta iron." I think confusion is avoided by sticking to the term "alpha iron." The diffusing element has passed into solid solution in the iron and the chemical analysis of the crystal is such that the alpha-iron solid-solution crystal is easily affected by temperature and the grain will grow abnormally. Many high-chromium irons, particularly where the chromium content is above 15 per cent, when subjected to high temperatures, will grow very large grains or crystals merely by the absorption of the boundary and adjacent crystals taking on like orientation. That is what has happened here; the crystal growing towards the center more readily than laterally, perhaps because the crystal is being fed along its cleavage planes which run substantially at 90° to the surface receiving the diffusing element. As long as the high

temperatures now used in the process of diffusion are maintained, and the hours necessary to produce such diffusion, there will probably always be this undesirable grain growth accompanied by great brittleness. This undesirable feature accompanying diffusion can be modified of course, by mechanical work. Therefore it appears that diffusion coatings will find their principal application for those purposes where strength in the case is unimportant or where the part can be mechanically worked at high temperatures to break up this large structure. Subsequent heat treatment without mechanical work will not do it.

The high temperatures necessary to bring about diffusion, say for chromium, which is about 2300° F., can be lowered to probably in the neighborhood of 2000° F. by combining chromium with another element such as silicon. This brings me to a speculative question. It is true that silicon will diffuse in iron at about 2000° F., but chromium does not, or only very slightly. Now if chromium and silicon are used together, just why can a fair depth of case be produced at a temperature that is suitable for silicon and not chromium? I am of the opinion that the silicon and chromium combine, forming a chemical compound, which is diffused into the surface of the iron. Perhaps where chromium alone is employed there is a compound formed which is dissolved by the alpha iron. I am wondering whether the author has made any determinations along this line. I realize that it is not perhaps of great practical importance to determine whether diffusion takes place by the formation of a chemical compound prior to its being absorbed by the surface layer of the iron. As the theory of diffusion appears to embrace the exchange of atoms, chemical compounds are most likely readily formed, if this atomic exchange is the correct theory of the system of diffusion.

The core, perhaps, could be made up of an alloy iron whose transformation point is so high that even at the high temperatures now employed for diffusion, the core will exist as alpha or delta iron. I should expect diffusion to take place more rapidly with such a core material than with ordinary low-carbon steel wherein the carbon is in solution in the crystal at these temperatures.

R. RICKETT, Bloomfield, N. J. (written discussion).—Mr. Kelley is to be commended for his contribution to the important subject of diffusion in metals. The type of grain structure that he describes has been observed in connection with several processes involving diffusion and is fairly well known but apparently no one has previously offered an explanation of how these columnar grains are formed.

Mr. Kelley says that rapid grain growth accompanies the diffusion of one metal into another. The writer is of the opinion that the large grain size of the diffusion areas shown in Mr. Kelley's photomicrographs can be accounted for, in a large measure at least, by the surface decarburization of the samples and the subsequent rapid growth of the ferrite grains in the pearlite-free area, which would be expected at the high temperatures used. Results on Armeo iron heated in chromium support this contention. Figs. 11 and 12 show representative sections of structures obtained, the average grain size in the interior or "core" being as large or larger than that in the area of diffusion or the "case." Fig. 5 (Mr. Kelley's) also supports this view, the grains in the decarburized area increasing in size as the edge of the specimen is approached, presumably because the areas nearest the edge have been free from pearlite for a longer time and thus have had more opportunity to grow large grains.

Another feature brought out by a comparison of Figs. 11 and 12 (making allowance for the difference in magnification) is that on longer heating the columnar grains may grow in width as well as in depth. Some of the case grains in the sample shown in Fig. 12 were much wider than any appearing in the photomicrograph.

The sharp line usually found between the columnar-grained zone and the core is of considerable interest. As mentioned by Mr. Kelley, this line is associated with

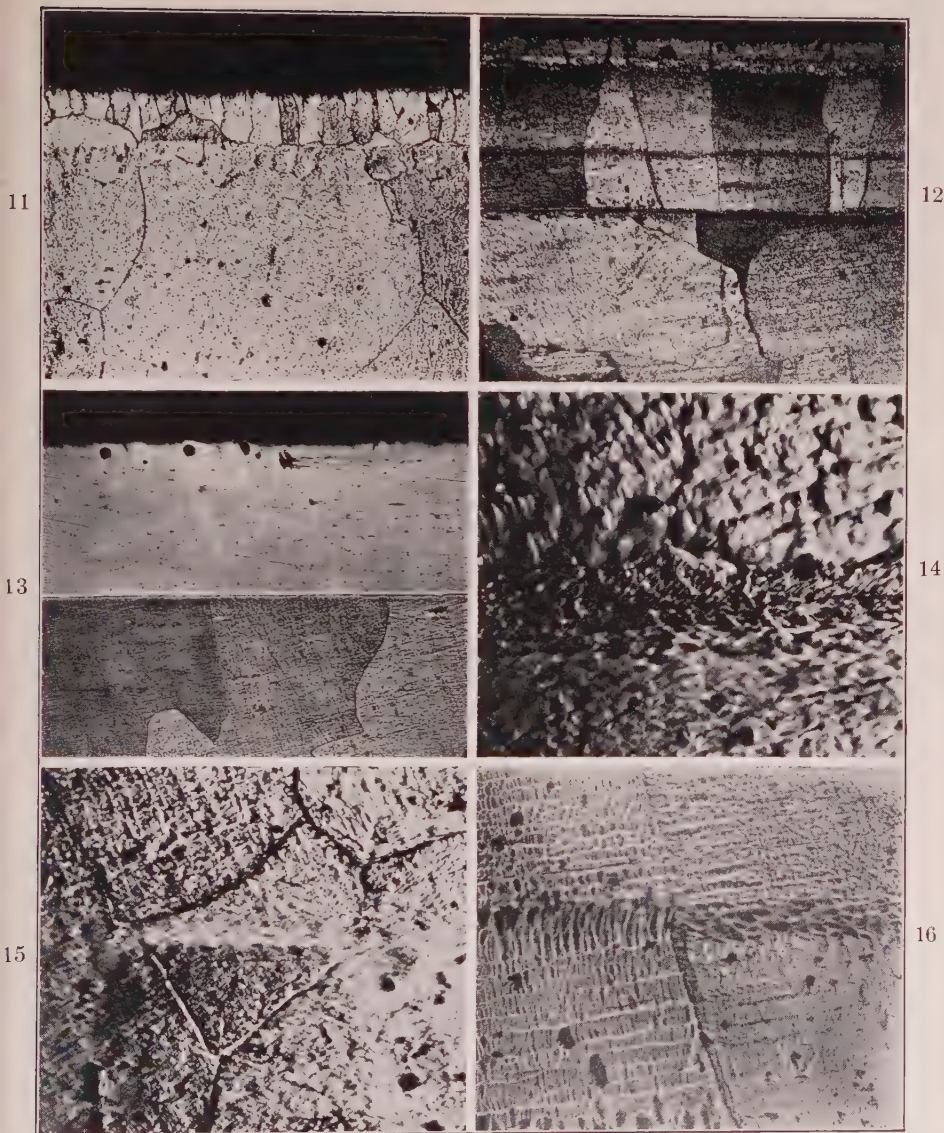


FIG. 11.—ARMCO IRON HEATED IN CHROMIUM. $\times 200$.

FIG. 12.—ARMCO IRON HEATED IN CHROMIUM TWICE AS LONG AS SAMPLE IN FIG. 11. $\times 100$.

FIG. 13.—SAME AS FIG. 12. ETCHED WITH 5 PER CENT. HNO_3 IN ALCOHOL. $\times 100$.

FIG. 14.—SAME SPECIMEN AS IN FIG. 12. BOUNDARY BETWEEN ZONE OF COLUMNAR GRAINS AND INTERIOR. $\times 1500$.

FIG. 15.—SAME SPECIMEN AS IN FIG. 11. BOUNDARY BETWEEN CASE AND CORE. $\times 1500$.

FIG. 16.—SAME SPECIMEN AS IN FIG. 12. DARK LINE ACROSS COLUMNAR GRAINS. $\times 400$.

(Reduced to 65 per cent. original scale; original magnifications given.)

a sharp falling off in the rate of diffusion, a fact that is further demonstrated by suitable etching reagents. Fig. 13 shows the same specimen as Fig. 12 after etching with nitric acid in alcohol, which readily etches the core but does not attack the outside region. In Fig. 11, this line of demarcation appears light in the photograph but in this specimen also it marked the outside limit of the area that could be etched with nitric acid. It should also be noted that the grains outside this line in Fig. 11 are not all columnar. In order to get more information on the nature of this boundary line, it was studied at higher magnification. Fig. 14 shows a boundary between the case and the core of the specimen shown in Fig. 12, the magnification being 1500 dia. It is seen to consist of at least two distinct zones differing in orientation from each other and from the adjacent grains of the case and core. Few distinct grain boundaries could be distinguished in these narrow layers, these few being continuations of the boundaries between larger adjacent grains and never extending through more than one of the narrow zones. Fig. 15 shows the light boundary shown in Fig. 11, at a section where it crosses what might be thought a single grain from its outline, but which can be seen to have different orientations on the two sides of the boundary. It may well be, therefore, that this boundary between case and core represents a region of changing orientations of the grains as suggested by Mr. Kelley.

Fig. 12 also shows a dark band across the surface of the columnar grains. Fig. 16 shows that this band does not represent a change in orientation, although it does apparently represent a fairly sharp change in composition since the structure on either side could be developed alone by suitable etching reagents.

C. BENEDICKS, Stockholm, Sweden (written discussion).—The observations of this paper are very interesting, but the assumption of a special "force of diffusion" needs some further analysis.

The most fundamental way of growing large crystals is of course the following: If the substance occurs as a definite, say liquid, phase and a new (solid) phase is formed slowly from one direction, this forms large crystals (presenting a main growth direction determined by the temperature gradient). Things are quite similar in the case of the primary phase being likewise solid, the substance therefore possessing allotropy.

Now, iron possesses an allotropic ($\alpha \rightleftharpoons \gamma$) point, A_3 , at about 900° , which is acted upon in two different ways by added substances.⁶ (1) Those having an atomic lattice similar to that of α Fe are known to raise A_3 —even so much as to coincide with A_4 —at 1400° . To this group belong Cr, Mo, W; Si and Sn act in the same way, being more soluble in α than in γ Fe. (2) Those which are more soluble in γ Fe than in α Fe and therefore lower A_3 . To this group belong C, Mn, Ni.

Suppose, then, that a specimen of iron is embedded in a powdered substance belonging to one of these groups, and heated to a high temperature beyond A_3 . Let us first admit that the substance belongs to the first group; *e. g.*, Cr. Then the following will happen. The iron specimen being in its γ state, though at a slow rate, will dissolve an increasing amount of Cr. When the γ surface layer has thus been saturated with Cr, a new phase will appear, *viz.* α Fe, containing dissolved a somewhat higher (minimum) chromium content; then the chromium concentration of the α phase will increase.

Now, as easily understood from the fact referred to at the beginning, this α phase, growing slowly from the surface of the specimen inwards, will give rise to large crystal grains, elongated in the direction of the growth of the α phase. This is precisely what has been so well borne out by Mr. Kelley, for Cr, Si, Sn and Mo.

Let us then admit that the substance belongs to the second group; *e. g.*, carbon. The γ iron, of course, will dissolve an increasing amount of carbon, but this will cause

⁶ C. Benedicks: Metallographic Researches, 70. New York, 1926. McGraw-Hill Book Co.

no α phase to appear, the stability of γ Fe only increasing by the carbon addition. Consequently, in this case, the diffusion of the carbon, taking place from the surface inwards, causes no new Fe phase to appear, and it will therefore leave the crystal grains essentially unchanged. This fact is evidenced by the very old case-cementing experience, where no columnar crystals are observed. It is further well borne out by Mr. Kelley's statement that the iron at 1350° "does not take up the nickel," which evidently must be interpreted as stating that iron does not take up nickel *so as to form a distinctly visible layer*. As a matter of fact, the dissolution of nickel in iron is theoretically quite as necessary as the dissolution of iron in nickel—a fact clearly expressed by point 5, quoted from Grube. The only thing is that no essential change of the crystal grains will be brought about by the nickel—like carbon—diffusing through the γ iron.

Against this theory, however, could be objected that Fig. 7 gives evidence of the formation of a very distinct surface layer when using Mn—a substance belonging to the second group, which should consequently cause no phase to appear. The fact is, however, that this case is very easily explained. As a matter of fact, the firing in this case was made at 1250° C., which is above the melting point of Mn (say 1225°). Hence Mn—owing to its rather high volatility—will easily form a comparatively thick fluid layer on the surface of the Fe specimen. The large holes occurring in the surface layer (Fig. 7) support the view that this layer has been in a fluid state. Inside the Fe specimen the Mn has occasioned very little change, as must be expected. If on the other hand, the firing is effected at a temperature below A_3 , the following items may be mentioned:

Heating Fe in a substance of the second group—*e. g.*, carbon—will then cause the α iron to be transformed on the surface into a γ layer, growing slowly inwards. This cementation at *too low a temperature* probably will cause a layer of columnar crystals to appear. The writer does not know whether some observations are at hand in this direction.

Suppose, instead, the specimen to possess a considerable carbon content—say 0.9 per cent—and to be exposed, below A_3 , say at 850° , to a decarburizing agent. In this case the bulk of the specimen is in the γ state but the decarburization will cause the surface layer to be transformed into an α phase, slowly growing inwards. Consequently, conditions will be favorable for a considerable grain growth in the surface. This apparently is explanation of the structure seen in Fig. 9.⁷

An interesting item is the question whether the speed of diffusion in a given grain may be said to be a vectorial quality of the grain. An apparent support of this supposition might be afforded by the fact that several grains of the surface layer project much farther inwards than most of the others (Figs. 3 and 4). It must be kept in mind, however, that this item may be due simply to the fact of a given γ grain below the α layer having such a position as to change easily into the α lattice of an approaching columnar grain: it will be absorbed by this earlier than would be the case otherwise and will start by having a lower content of the diffusing substance than otherwise.

It will be seen from this analysis of the observations given in the paper that the "force of diffusion" introduced by the author may be said to have the following significance: Diffusion taking place in a specimen will alter its concentration. This may cause a new phase to appear at the surface. When this new phase increases slowly in the inward direction, it will give rise to comparatively large columnar grains. On the

⁷ In this case the grain growth tendency due to decarburization would vanish at a temperature below A_3 as then no new phase may be formed. Even in this case, however, a certain though much weaker growth tendency might occur, due to the fact that a purer metal generally has a slightly higher crystallization tendency than an impure metal—an item which was not necessary to consider previously.

contrary, if no new phase is formed, diffusion has not been found to exert any inducement towards a rapid grain growth.

It would be interesting also to discuss the dark boundary line appearing on the photos; this, however, can scarcely be done with any advantage without examining the specimens themselves or having photos focused differently. A tendency to form a double line might possibly be referred to a slight growth, occurring during the cooling down.

Interatomic Forces in Metals and Alloys

BY ROBERT F. MEHL,* PH. D., ANACOSTIA, D. C.

(New York Meeting, February, 1928)

THE mechanical behavior of metals and alloys is presumably conditioned by two factors; namely, the crystalline symmetry and the interatomic forces. Considerable attention has been given to the first of these factors through the recent advances in X-ray technique. It is the purpose of the present paper to call attention to the importance of the second of these factors, to point out promising methods of investigation, and to present some pertinent data.

Plastic deformation takes place by slip along atomic planes.¹ This slip may be inhibited in a number of ways: by the interatomic forces of cohesion which bind the atoms rigidly in a lattice structure, which in pure metals is usually of high symmetry; by lattice distortion caused by solid solution formation or by mechanical strain; by the intercrystalline boundaries where slip is restrained, probably by the non-registration of the atom planes in adjacent crystallites;² and by the presence of small hard particles which serve to "key" the slip along the atom planes.³

In pure metals, and perhaps also in solid solutions, the atom planes of easiest slip are those exhibiting the greatest density of atomic population and the greatest interplanar distance⁴ and apparently can now be predicted from the analysis of the lattices. Concerning the interatomic forces, which resist this slip by holding the atoms firmly together, little is known.

Most textbooks on physical metallurgy, following the work of Bortone,⁵ correlate the hardness of the pure metals with the atomic volume,

* Superintendent of Division of Physical Metallurgy, Naval Research Laboratory.

¹ A number of generalizations of this sort appear in the present paper. They have been so completely absorbed by metallurgical literature that no specific reference to original papers need be given. In each case they are stated so axiomatically that no mistake can be made concerning their originality.

² Dean and Gregg have proposed that the greater rigidity at the grain boundary may be explained by an electron displacement somewhat similar to that occurring in chemical compounds. This conception is interesting in a number of ways in connection with the discussion in the present paper. R. S. Dean and J. L. Gregg: *Proc. Inst. Met. Div., A. I. M. E.* (1927) 368.

³ This is, of course, a brief statement of the slip-resistance theory of hardness, more completely given elsewhere by Zay Jeffries and R. S. Archer [*Chem. & Met. Eng.* (1921) **24**, 1057].

⁴ W. P. Davey: *Trans. Am. Soc. Steel Treating* (1924) **6**, 375.

⁵ S. Bortone: *Chem. News* (1873) **27**, 215.

with which it stands in inverse proportion. This parallelism is striking, but not especially illuminating. The atomic volume may be considered as the result of the intensity of the cohesive forces. Those elements like sodium, which have great atomic volumes may be inferred to have rela-

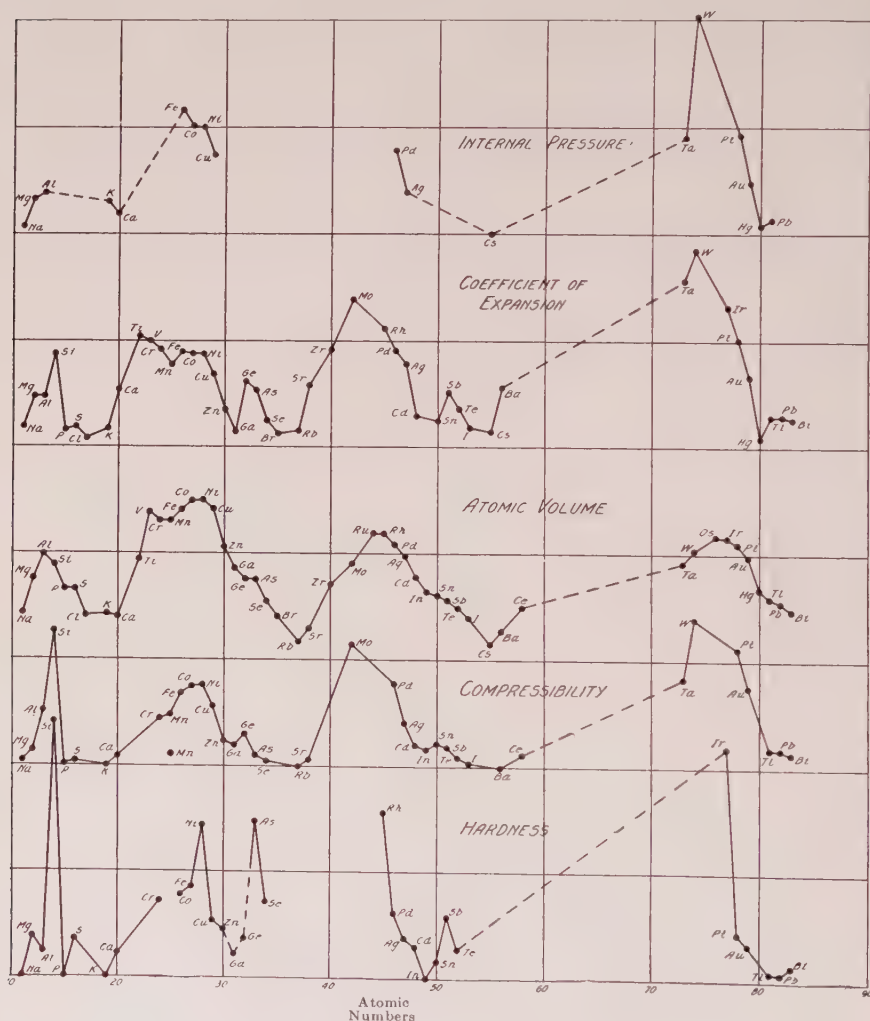


FIG. 1.—PERIODIC PROPERTIES OF THE METALS.

tively weak atomic fields of force, whereas elements like tungsten, which have small atomic volumes, presumably have relatively intense atomic fields of force. The atomic volume, therefore, is rather a result of the interatomic forces than a measure of it, though the distinction is not rigorous. However, there is a correlation more direct than that by means

of the atomic volume; namely, by means of compressibility and the concept of internal pressure.⁶

The hardness of the pure metals was investigated in 1900 by Rydberg,⁷ who measured the scratch hardness of 36 elements based on Moh's scale. Plotted according to atomic numbers, these show a surprising periodicity closely paralleling the reciprocal atomic volume curve, and also the reciprocal compressibility curve, and the internal pressure curve (Fig. 1). A similar hardness curve was obtained much later by Edwards,⁸ who measured the Brinell hardness on materials of a purity probably superior to that of those used by Rydberg.

IMPORTANCE OF COMPRESSIBILITY IN BEHAVIOR OF SOLIDS

The importance of compressibility⁹ in determining the existence and behavior of solids has been repeatedly emphasized by T. W. Richards,¹⁰ who has correlated the property with his equation of state for solids, which in abbreviated form¹¹ is

$$p + \pi_0 = \pi_p + P_\theta \quad (1)$$

where p is the external pressure, π_0 the intrinsic cohesive force, π_p the intrinsic expansive force, and P_θ the thermal expansive force. The left-hand members of the equation are therefore cohesive pressures and the right-hand members expansive pressures which at equilibrium for any solid are balanced.

The application of the concept of pressure to solids perhaps is scientifically somewhat questionable, since pressure ordinarily means the summation of the force effects of impinging moving atoms or molecules over a unit of surface, and there is no analogous behavior in solids. (It

⁶ John Johnston [A Correlation of the Elastic Behavior of Metals with Certain of Their Physical Constants. *Jnl. Am. Chem. Soc.* (1912) **34**, 788] developed a thermodynamic basis for the elastic behavior of the metals derived from a theory of partial melting during deformation, and showed certain periodic variations correlated with the periodic curve of the absolute melting points.

⁷ J. R. Rydberg: *Zeitschr. phys. Chem.* (1900) **33**, 353.

⁸ C. A. Edwards: *Jnl. Inst. Metals* (1918) **20**, 86. Apparently Edwards was unaware of Rydberg's work, for no reference is made to it in his paper.

⁹ Defined as the fractional volume change brought about by an increase of one unit of hydrostatic pressure. Mathematically the compressibility coefficient is given by $\beta = \frac{1}{V_0} \frac{dV}{dp}$ where V_0 is the original volume and $\frac{dV}{dp}$ the change of volume with pressure.

¹⁰ *Proc. Am. Acad. Arts Sci.* (1904) **39**, 603; *Jnl. Am. Chem. Soc.* (1914) **36**, 2417; *Jnl. Frank. Inst.* (1924) **198**, 25; *Chem. Rev.* (1925) **2**, 315.

¹¹ In extended form the equation is $p + \pi_0 \left(\frac{V_0}{V_1} \right)^m = \pi_p \left(\frac{V_0}{V_1} \right)^n + \frac{\alpha T}{\beta}$ in which the bracketed quantities are introduced to take account of the variation of the intrinsic cohesive and expansive pressures with volume and in which the last member, where α is the coefficient of cubic expansion and β the compressibility, replaces P_θ to which it is thermodynamically equivalent.

is, however, a well known fact that diffusion takes place in solids, even among atoms or molecules of the same kind—such as radioactive lead in non-radioactive lead.)

Ideally, only forces should be treated, but despite the great amount of work recently done on lattice energetics (especially by Born and his collaborators), the subject is still largely obscure. If it is kept clearly in mind that the conception of pressures in solids is but a convenient mode of expressing interatomic forces, adopted because many illuminating facts may be discovered by its use, and that pressures represent an average of the interatomic forces divided by the area, no confusion need arise.

Equation (1), then, is a convenient tool to be used in reasoning about the behavior of solids. If the lattice is a very rigid one, because of the intensity of the interatomic forces (or pressures), both π_0 and π_p will be great, and the atoms will be under a high state of compression. An increase in p , the external pressure, will, therefore, have only a small effect upon the volume; that is, the compressibility will be small, as with tungsten, which has a compressibility coefficient of 0.27×10^{-6} . If the interatomic forces (or pressures) are small, π_0 and π_p will be small and an increase in p will have a relatively great effect upon the volume; that is, the compressibility will be large, as with sodium, which has a compressibility coefficient of 15.6×10^{-6} . Therefore compressibility should be related to the intensity of the interatomic pressures or forces.¹²

A direct calculation of π_0 , the internal cohesive pressure, will give a more direct analysis of the interatomic forces, in certain cases more valuable than the compressibility data, as will be shown later.

It is interesting to compare the hardness numbers of the elements with their compressibilities. This has been done in Fig. 1, using Edward's Brinell hardness numbers and the best values for the compressibilities of the elements taken from the work of Richards¹³ and that of Bridgman.¹⁴

The pure metals are mostly intrinsically of high symmetry; only a few metals crystallize in lattices of low symmetry. In addition to the natural high symmetry of the metals, they are, when pure, inherently free from the type of lattice distortion which accompanies solid solution formation and that which is brought about by cold work. The resistance to slip should therefore be in the order of the interatomic forces, with

¹² It should be noted that the compressibility coefficients can be calculated from the lattice energetics, as has been done by Born [Der Aufbau der Materie, Julius Springer, 1922] and by Thompson [*Phil. Mag.* (1922) **42**, 721]. The values obtained agree fairly well with the observed values. However, in their application to compounds (and therefore to alloys) the results are less salutary [see T. W. Richards and E. P. R. Saerens: *Jnl. Am. Chem. Soc.* (1924) **46**, 946].

¹³ *Loc. cit.*

¹⁴ *Proc. Am. Acad. Arts Sci.* (1923) **58**, 166.

variations only where elements of very high symmetry are adjacent to elements of somewhat lower symmetry. In place of the actual interatomic forces, we may take compressibility, where these effects are most obviously patent.

The parallelism between the hardness curve and the reciprocal compressibility curve is striking (Fig. 1), and such deviations as occur are instructive.

It is to be noted that the group of elements from gallium to rubidium, and that from indium to cesium, form a maximum on the hardness curve which is not so strongly indicated on any other curve except that of the absolute melting point.¹⁵

FACTORS GOVERNING HARDNESS OF PURE METALS

Keeping in mind that the hardness of the pure metals is presumably conditioned by two factors, the interatomic forces and the crystalline symmetry, this lack of parallelism becomes explicable. The elements forming these two anomalous maxima on the hardness curve are all of relatively low symmetry, and possess relatively few planes upon which, by reason of the atomic populations and the interplanar distances, slip can easily take place. In the first of these, germanium is diamond-cubic and somewhat lower in symmetry than its neighbor gallium, which appears to be face-centered tetragonal. Arsenic is rhombohedral, and the selenium lattice is built up of screw-axes perpendicular to a trigonal basal plane, both lattices of low symmetry. In the second of these groups the elements antimony and selenium possess lattices similar to those exhibited by the two elements in the first group, in the same order. Tin is tetragonal. A similar anomalous behavior is shown by the elements lead and bismuth at the end of the curve, for though the compressibility of bismuth is greater than that of lead it is nevertheless harder. Bismuth is rhombohedral in structure, and therefore of an order of symmetry lower than lead, which is face-centered cubic. Magnesium falls higher on the hardness curve than would be expected from the compressibility or internal pressure. This can also be accounted for by a symmetry much lower than that of sodium and that of aluminum. Similarly, the great hardness of manganese may be attributed to its extraordinarily low symmetry. Bradley and Thewlis¹⁶ have shown that α manganese is cubic, $a_0 = 8.894\text{\AA}$., with 58 atoms in the unit cell. The structure is apparently that of a single body-centered cubic lattice, each lattice point replaced by a cluster of 29 atoms having tetrahedral symmetry.

¹⁵ The closer parallelism between the hardness curve and the curve of the absolute melting points than between the hardness curve and that of the reciprocal atomic volumes was pointed out by Edwards (*loc. cit.*) but he attempted no explanation.

¹⁶ A. J. Bradley and J. Thewlis: *Proc. Roy. Soc. (London)* (1927) **A115**, 456.

It appears, therefore, that the hardness of the elements can be described in terms of the interatomic forces, as measured by compressibility (or internal pressure) and by the number of planes of easy slip, as determined by the crystal structure. But it must be clearly kept in mind that this conclusion has been drawn for the parallelism of the periodic curves and for this reason applies only to elements nearly alike in atomic number. If a strict proportionality between compressibility (or internal pressure) and hardness be assumed for elements crystallizing in the same crystal system, several exceptions will appear.

TABLE 1.—*Values for Face-centered Cubic Metals*

Element	Atomic Number	Brinell Hardness	Internal Pressure in Kilomegabars	Reciprocal Compressibility $\frac{1}{\beta} \times 10^6$
Pb	82	6.95	72	0.422
Ca	20	22.0	95	0.1756
Al	13	24.7	191	0.75
Ag	47	37	208	1.00
Au	79	33	243	1.73
Cu	29	86	376	1.39
Pd	46	61	396	1.93
Pt	78	44	465	2.78
Ni	28	144	508	1.89
Co	27	86	510	1.85

Table 1 represents the separate values for Brinell hardness, internal pressure and compressibility for the face-centered cubic metals. The lack of proportionality is clearly evident. The conclusion seems inescapable that there is a factor operative in addition to the crystal symmetry (the type of lattice) and the interatomic forces. The nature of this factor is obscure, but it is very likely related to the distribution of forces around the atom periphery, and probably also to the position of the valence electrons with respect to the crystallographic axes. This would introduce a variety of slip resistance largely independent of the crystal-line symmetry. This factor does not appear to have been taken into account by previous writers. In elements near each other in atomic numbers the extranuclear electrons are nearly equal in number, and possible variations in the distribution of forces around the atom periphery are small, but not absent, as is indicated by the case of nickel and cobalt in Table 1.

Since cubic compressibility is an average of the linear compressibilities along the various crystallographic axes, it is not to be expected that the crystal symmetry should have any effect upon the compressibility curve, and the same may be said of the atomic volume. The striking parallelism between the curve of the absolute melting points and the hardness

curve in the regions of the anomalous maxima suggests that the melting point is similarly affected by the crystalline symmetry.

COMPRESSIBILITY AS MEASURE OF INTERATOMIC FORCE

Since it is evident that a variation in the interatomic forces will produce an alteration in the compressibility, this property may be taken as a criterion for the changes in interatomic forces affecting hardness. The peculiar metallurgical virtue in compressibility as a method of analysis of hardness lies in the fact that it is not appreciably affected by any mechanical deformation performed upon the material examined, and is therefore independent of grain-size conditions. Thus Bridgman¹⁷ found that severely cold-rolled copper and iron gave nearly the same values for compressibility as annealed copper and iron. This significant experiment demonstrates the essential identity of cold-worked and annealed metal, and is difficult to reconcile with the presence of amorphous metal in any considerable quantity, since an amorphous phase should have a considerably higher compressibility.¹⁸

From the finite value of the compressibility coefficient it is obvious that the concept of atomic volume as a property characteristic of a metal atom attending the metal atom unchanged in its alloys cannot be maintained. It must be clearly borne in mind that the radius of an atom is a function of the force field in which it occurs. This is obviously true¹⁹ and is of importance in connection with the theories of the hardness of solid solutions.

Though the symmetry factor is subordinate in the hardness of the pure metals, it is of first importance in the hardness of solid solutions. It has frequently been pointed out²⁰ that the hardness of solid solutions is caused, at least in part, by lattice distortion, which can be studied by X-ray diffraction. It has also been realized that the attraction between unlike atoms in a solution results in an increase in the cohesive forces, resulting in a greater hardness,²¹ but no attempt has been made to evaluate the relative magnitudes of these two factors.

In a solid solution of two metals normally crystallizing in the same space lattice in which equivalent atomic substitution obtains, the decrease

¹⁷ *Proc. Am. Acad. Arts Sci.* (1909) **44**, 265; (1923) **58**, 168.

¹⁸ Perhaps it should be remarked that the hydrostatic pressure used in the determining of compressibility has no effect upon the microstructure of the metal measured [Zay Jeffries: *Jnl. Inst. Metals* (1917) **18**, 243].

¹⁹ An analytical proof of this has been given by Bridgman: *Proc. Am. Acad. Arts Sci.* (1923) **58**, 227.

²⁰ See especially, W. Rosenhain: *Chem. & Met. Eng.* (1921) **25**, 243 and Zay Jeffries and R. S. Archer: *Chem. & Met. Eng.* (1921) **24**, 1057; (1923) **29**, 923, 966.

²¹ Zay Jeffries and R. S. Archer: *Science of Metals*, 232, 243, 260, 270, 396, 412. McGraw Hill, New York, 1924.

C. H. Desch: *Trans. Far. Soc.* (1914) **10**, 251.

in compressibility from the rule of mixtures value may be taken as a measure of the chemical attraction of the unlike atoms, and of course also as a measure of the increase in the lattice rigidity. In solid solutions where one atom of the solute replaces more than one atom of the solvent (as with Cu-Sn) and in solid solutions of metals normally crystallizing in different space lattices it is not possible to make a strict comparison between the observed compressibility and the rule of mixtures value, since the state of condensation of the solute atom in the alloy differs from that in the element. In such cases the change in compressibility perhaps cannot strictly be taken as a quantitative measure of the increased cohesive forces, though the data on compressibility must nevertheless be of fundamental importance.

COMPRESSIBILITY OF ALLOYS

An investigation of the compressibility of alloys has recently been carried out by the author.²² In order to make a preliminary survey of the field, a number of typical alloys were chosen.²³ The results of the investigation are given in Table 2. The calculated compressibility is obtained from the compressibilities of the component metals on the basis of the volume percentage composition.

Alloy No. 1 may be taken as an example of a solid solution in which simple substitution obtains and in which there is little chemical difference between the component metals (nickel and copper) and also in which the lattice constants are nearly equal (a_0 for Cu = 3.597, for Ni = 3.499). The compressibility coefficient found, therefore, is nearly equal to that calculated, the difference being but 3 per cent. The density is still less affected.

Alloy 2 is "Invar." Its compressibility coefficient is much higher than that calculated from nickel and α iron, and seems to indicate that the γ iron present possesses a much higher compressibility²⁴ than α iron.

Alloy 3 is an aluminum bronze in the α field near the limit of solid solubility. The 12 per cent. decrease in compressibility coefficient is paralleled by a 2.8 per cent. increase in density. Alloy 4 is a β solid solution, and shows a 19 per cent. decrease in compressibility, paralleled by a 5.4 per cent. increase in density. The β solid solutions in general are harder than the α ; in the case of the β solid solution in the Cu-Al

²² With collaboration in the experimental part by B. J. Mair. See *Jnl. Am. Chem. Soc.* (1928) **50**, 55.

²³ These alloys were very kindly prepared and treated by a number of industrial metallurgists. Acknowledgment for this valuable assistance has been made in the paper in the *Journal of American Chemical Society* referred to above.

²⁴ The compressibility of γ iron at room temperature could be roughly estimated by measuring the compressibility of a series of alloys with increasing percentage of iron and extrapolating over the α field to pure γ iron.

TABLE 2.—*Compressibility Data on Alloys*

Alloy Number	Composition, Per Cent.										Compressibility			Density		Increase, Per Cent.		
	Cu	Ni	Mn	Fe	C	Si	Cr	Al	Zn	Pb	Sn	Mg	Obs.	Compressibility			Calc.	Obs.
														Calc.	Decrease, Per Cent.			
1	55	44	1										0.62	0.64	3	8.910	8.901	0.1
2		36.77	0.49	63.24	0.15	0.15	0.05						0.85			8.402	8.206	
3	92.34							7.66					0.78	0.89	12	7.847	7.582	2.8
4	87.1							12.9					0.79	0.98	19	7.244	6.870	5.4
5	81.94			0.05					17.95	0.06			0.75	0.94	20	8.669	8.545	1.5
6	64.27			0.03					35.61	0.09			0.80	1.13	29	8.426	8.200	2.8
7	51.43			0.04					48.57	0.06			0.93	1.26	26	8.291	7.960	4.2
8	88.53			0.03							11.44		0.84	0.89	6	8.631	8.710	-0.9
9	61.16			0.06							38.78		0.98	1.23	20	9.024	8.210	9.9
10	67.43			0.04							32.53		0.89	1.17	24	8.913	8.320	7.0
11				0.12		0.09		87.24				12.56	1.55	1.68	8	2.553	2.474	3.2
12					0.89	Remainder	Armco iron						0.61			7.798		
13	Same as No. 12												0.61			7.835		
14					1.35	Remainder	Armco iron						0.83			7.799		
15	Same as No. 14												0.85			7.807		

system superior cohesive forces apparently favor an increased hardness, though doubtless a lower symmetry contributes largely.

Alloy 5 is an α -brass half saturated. The decrease in compressibility is 20 per cent., which is paralleled by a density increase of 1.5 per cent. Alloy 6 is an α brass, nearly saturated. This composition shows a decrease in compressibility of 29 per cent. paralleled by a density increase of 2.8 per cent. It is evident from these figures that the copper and zinc atoms in the α brasses are much more tightly packed than in the pure metals, and the cohesive forces are accordingly greater. These brasses will be again considered in connection with internal pressures.

Alloy 7 is a β brass. The decrease in the compressibility, 26 per cent., appears less than that in the case of the α brasses. The superior hardness is therefore to be accounted for by the lower symmetry.²⁵

Alloy 8 is an α solid solution, nearly saturated, in the copper-tin system. Despite an apparent decrease in density, and the fact that Weiss²⁶ found that one atom of tin replaces several atoms of copper, the compressibility decreases 6 per cent. Alloy 9 is the compound Cu_3Sn and shows a decrease in compressibility of 20 per cent. and a density increase of 9.9 per cent. Alloy 10 is the δ solid solution and shows a decrease in compressibility of 24 per cent. and a density increase of 7.0. The occasional lack of parallelism between density and compressibility in alloys is very evident in this system.

The cohesive forces in the δ solid solution are presumably greater than in the compound Cu_3Sn . The Brinell numbers of the two alloys are in the same order,²⁷ but it is claimed that the compound Cu_3Sn shows the greater scratch hardness.²⁸

Alloy 11 is in the $\alpha + \beta$ field in the aluminum-magnesium system. It shows a decrease of 8 per cent. in compressibility as compared to a density increase of 3.2 per cent.

In general it may therefore be said that the compressibility of an alloy may be taken as an approximate measure of the superior cohesive forces in alloys. With solid solutions of like metals these cohesive forces are only slightly greater (as with copper and nickel) but with solid solutions of metals differing widely in chemical and crystallographic type the difference may be considerable. No case has been found in which there is an increase in compressibility.

Compressibility of Steels

The results of the measurements on the steels are of especial interest. If we assume that the superior hardness of alloys is caused by (1) increased

²⁵ Owen and Preston [*Proc. Phys. Soc. (London)* (1923-24) **36**, 49], among others, showed that β brass is body-centered cubic.

²⁶ Weiss: *Proc. Roy Soc. Lond.* (1925) **108**, 643.

²⁷ Bauer and Vollenbruck: *Zeitschr. für Metallk.* (1924) **16**, 426.

²⁸ International Critical Tables, **2**, 561.

cohesive forces, and (2) by slip-resistance factors of a purely crystallographic nature (the first factor may be conveniently named "chemical hardness" and the second "physical hardness"), the hardness of the steels may be analyzed in an interesting way. It is tacitly assumed by most writers on the subject that martensitic hardness is caused by the second of the two factors—namely, purely crystallographic slip-resistance—and controversy has largely concerned itself with the particular nature of this factor. The present investigation throws no direct light on this question, but indirectly may be of value in furnishing a definite statement regarding factor (1).

Alloy 12 is a pure iron-carbon alloy, with 0.89 per cent. carbon and an Armco iron base. Its compressibility after quenching from 900° C. in cold water was 0.61×10^{-6} . After a thorough annealing treatment, which rendered the alloy pearlitic, the compressibility was again 0.61×10^{-6} , although the Brinell hardness had fallen from 641 to 241. Alloy 14 is a hypereutectoid alloy in the same system, with 1.36 per cent. carbon and an Armco iron base. Its compressibility after quenching was 0.83×10^{-6} , and after thorough annealing 0.85×10^{-6} , within the possible error identical with the first.

It appears therefore that despite the great increase in hardness brought about by quenching, no appreciable increase in the cohesive forces is obtained. It is very surprising that a glass-hard steel should be as compressible as an annealed pearlitic steel, yet regarded from the viewpoint of the slip-resistance theory of hardness as applied to the steels,²⁹ the result is not strange. The results on the compressibility of the carbon steels are in complete accord with this theory, for the theory assumes that the superior hardness of the quenched steels is caused by a particular mechanical arrangement of the structural units present also in annealed steels; namely, ferrite and cementite. It is highly probable, from the apparent identity of the compressibility values for the steels in the quenched and annealed conditions, that the structural *units* in quenched steel are not greatly different from those in annealed steel, and this seems to indicate that the martensite is largely ferrite and finely divided cementite, differing from pearlite only in the size and arrangement of the ferrite and the cementite grains.

Variations in grain size and in the state of mechanical strain appear to make little difference in compressibility, judging from the experiment by Bridgman³⁰ discussed earlier in this paper, so that an increase in hardness caused by either of these two effects would have little effect upon compressibility. On the other hand, lattice distortion, which has been postu-

²⁹ Modern opinion on this point has recently been summarized by A. Sauveur: *Trans.* (1926) **73**, 859.

³⁰ Bridgman: *Proc. Am. Acad. Arts Sci.* (1909) **44**, 265; (1923) **58**, 168.

lated as a cause of hardness in martensite, could be produced only by an alteration in the interatomic forces, and this should result in an appreciable compressibility difference. In this connection the results here presented throw some light on the Hanemann-Schrader theory.³¹

In this it is assumed that there is an *epsilon* and an *eta* phase in equilibrium with austenite, and that the *eta* phase produces the martensitic hardness by virtue of its content of an iron carbide, Fe_{24}C . It is assumed that the "hardness of martensite" is "caused by a definite arrangement of the iron and carbon atoms in an iron-carbon compound" (Fe_{24}C), and that this compound is hard because of the lack of symmetry of its space lattice and the lattice forces which inhere in it.

The results of the compressibility measurements limit the possible interpretations of this theory. The inherent superior hardness of the hypothetical compound Fe_{24}C must be explained by either (1) an extraordinarily low symmetry or (2) interatomic forces between the iron and carbon atoms very much greater than those in austenite or pearlite, or by both (1) and (2). X-ray investigation of the steels seems to show that there is no great quantity of a constituent of low symmetry, since only face-centered cubes characteristic of γ iron and body-centered cubes characteristic of α iron (and perhaps a certain amount of a tetragonal lattice), both lattices of high symmetry, have been found. The alternative (2) seems definitely denied by the compressibility measurements, which show no appreciable increase in the cohesive forces. It is not impossible, of course, that there should be small quantities of a carbide such as Fe_{24}C in quenched steel, but the only large contribution it could make to the superior hardness of martensite would be by virtue of a very fine state of subdivision. In such a form the Hanemann-Schrader theory is nearly indistinguishable from the more generally accepted slip-resistance theory, and in the assumption of the presence of an unknown compound of iron and carbon seems much less likely.

CONCEPT OF INTERNAL PRESSURES

The interatomic forces in alloys can be studied in another way, as suggested at the beginning; namely, by the use of the concept of internal pressures.³² The internal pressure is π_0 in Equation (1). Richards³³ has shown that it may be approximately evaluated by the expression

$$\pi_0 = \frac{R}{V_A \alpha_s} \quad (2)$$

³¹ *Trans. Amer. Soc. Steel Treating* (1926) 9, 229.

³² Internal pressures have been studied by a number of investigators, including I Traube, C. Benedict, G. Tammann, but especially T. W. Richards.

³³ *Loc. cit.*

where R is the gas constant, V_A the atomic volume, and α_s the coefficient of cubic thermal expansion.³⁴

Traube³⁵ has shown that internal pressures calculated in this way give values for the pure metals which closely parallel the scratch hardness values given by Rydberg. In general, therefore, internal pressures may be taken as a measure of the intensity of the attraction (and repulsion) between the atoms in solids, much as compressibility.³⁶

This calculation can be applied to alloys in order to evaluate the chemical attraction factor between the unlike atoms. It requires knowledge of the mean atomic volume and the coefficient of thermal expansion only. Until a short time ago there were almost no trustworthy data on pure binary alloys with comparable data for the pure component metals. Recently, however, C. H. Johansson³⁷ measured α_s for alloys of the systems silver-gold, copper-nickel, silver-palladium, copper-palladium, copper-gold, and gold-palladium. From these the author has calculated the internal pressures and compared the calculated values with the rule of mixtures values.³⁸ In each case an increase in the internal pressure is found, resulting from the attraction between the unlike atoms. For the system silver-gold the maximum increase is 2 per cent., for copper-nickel 4 per cent., for silver-palladium 16 per cent., for copper-palladium 10 per cent., for copper-gold 6 per cent., and for gold-palladium 12 per cent.

These results are interesting in connection with the hardness of the solid solutions investigated by Johansson. High-grade data on hardness are available only for the systems copper-nickel, silver-gold, and gold-copper. These have been determined by N. S. Kurnakov and C. Czernuszny, using the scratch method.³⁹

Fig. 2 represents the *increase* in hardness of the alloys over the rule of mixtures values plotted against composition, and also the increase in the internal pressures, for the system silver-gold. Since the internal pressures closely parallel the hardness numbers for the pure metals, it may be assumed that the relative positions of the two curves give a semi-quantitative analysis of the factors involved in the hardness of these solid solutions. For the system silver-gold the internal pressure shows an

³⁴ T. W. Richards recently [*Jnl. Am. Chem. Soc.* (1926) **48**, 3063] proposed a modification of the above equation which he regards as more exact, namely

$$\pi_0 = \frac{n'}{n' - m} \times \frac{R}{V_A \alpha_s},$$
 in which n' and m are the exponents of the volume quantities in an abbreviated form of the equation given in Footnote 11.

³⁵ I. Traube: *Zeitschr. anorg. Chem.* (1903) **34**, 413.

³⁶ The mathematical relation between compressibility and internal pressure has been derived by T. W. Richards: *Jnl. Am. Chem. Soc.* (1926) **48**, 3063.

³⁷ *Ann. d. Physik.* (1925) **76**, 445.

³⁸ R. F. Mehl: *Jnl. Am. Chem. Soc.* (1928) **50**, 73.

³⁹ *Zeitschr. anorg. Chem.* (1907) **54**, 164; (1908) **60**, 16.

increase of but 2 per cent. whereas the hardness increases 104 per cent. It appears therefore that only about one-fiftieth of the superior hardness of these solid solutions is contributed by the attraction between the unlike atoms. The remainder is probably contributed by lattice distortion and electron displacement resulting in a field of force around the metal atoms less symmetrical than those existing in the atoms of the pure component metals.

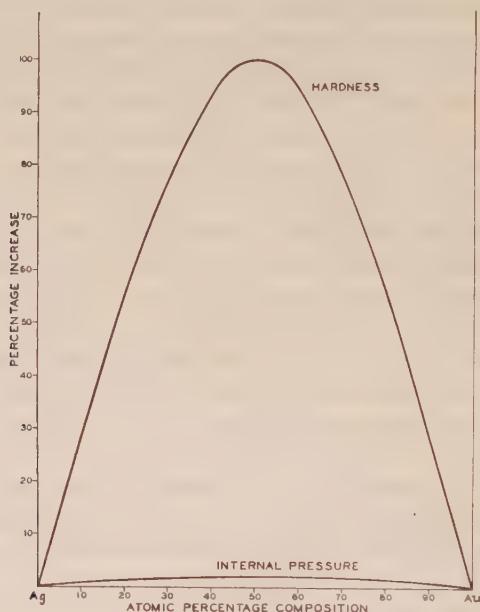


FIG. 2.—HARDNESS AND INTERNAL PRESSURE IN THE SYSTEM SILVER-GOLD.

Similar calculation for the copper-nickel system gives an increase of 4 per cent. in the internal pressure as compared to 63 per cent. in hardness, and for copper-gold system 6 per cent. as compared to 100 per cent.

The data of P. Hidnert⁴⁰ on the coefficient of thermal expansion of the brasses afford a similar calculation for these alloys, such as given in Table 3.

The increase in hardness in the α brasses is surprisingly small as compared with the increase in internal pressure and the decrease in compressibility, and it appears that some factors which induce hardness in pure component metals are no longer fully operative in the α brasses. It must be remembered in connection with this that the zinc atoms in α brass do not crystallize on the normal triangular close-packed lattice. The observation of C. F. Elam⁴¹ that a single crystal of α brass will

⁴⁰ Bureau of Standards *Sci. Paper* 410 (1922).

⁴¹ *Proc. Roy. Soc. (London)* (1927) **115A**, 133.

TABLE 3.—*Calculations on the Alpha Brasses**

Weight Percentage Copper	Decrease in Specific Volume, Per Cent.	Decrease in Compressibility Per Cent.	Increase in Internal Pressure, Per Cent.	Increase in Hardness, Per Cent.
100.0				
90.0	1.05	13	4.2	10
80.0	1.71	21	11.9	18
70.0	2.49	26	16.5	22
63.0	2.95	30	20.0	23

* The specific volume has been calculated from the densities of the brasses; the compressibilities have been calculated from the data in Table 2; the hardness numbers have been calculated from the data of Harris: *Jnl. Inst. Metals* (1922) **28**, 327.

elongate 160 per cent. as compared to 60 per cent. for a single crystal of copper may in some way be related to the fact that the increase in hardness of the α brasses is about the same in magnitude as that of the decrease in compressibility and the increase in internal pressure, that is, the usual additional factor of slip resistance of a purely crystallographic nature seems here to be negligible.

It is generally held that the hardening induced by a solute metal is in direct proportion to the accompanying distortion, and that the amount of distortion depends on the difference in the atomic volumes of the solute and solvent atoms.⁴² It is very unlikely, however, that the case can be so simple. The atomic volumes of silver and gold are nearly identical (10.28 and 10.22, respectively) but the hardness of the intermediate alloys reaches a value 100 per cent. greater than that of the average value of the two component metals. As stated in the foregoing, it is not permissible to assume the atomic volume of an atom as a characteristic property accompanying an atom unchanged in alloys. The atomic volume is a partial function of the force field which is imposed upon the atom. The internal pressure of gold is 238 kilomegabars while that of silver is 199 kilomegabars. The internal pressure of a 10 atomic per cent. silver alloy is 233 kilomegabars, which must mean that the silver atom in this solid solution is subjected to a pressure of 34 kilomegabars in excess of that obtaining in pure silver. This should result in a smaller atomic volume for the silver; and conversely a large atomic volume for the gold. In alloys of gold and silver, therefore, the atomic volume of silver tends to become less than 10.28 and the atomic volume of gold

⁴² F. C. Thompson [*Trans. Far. Soc.* (1917) **12**, 23] designated the difference in the atomic volumes as the controlling factor in the hardness of solid solutions. A. L. Norbury [*Trans. Far. Soc.* (1924) **19**, 586] showed that the hardening power of a member of metals in α solid solution with copper is proportional to the difference in size of the solvent and solute atoms, though silicon in copper was exceptional (and also sodium in lead).

tends to become greater than 10.22. It is evident, therefore, that the difference in the atomic volumes of the metals in the pure state must not be taken as sufficient to define the degree of roughening of the slip planes, but that the variations in the interatomic forces which control the atomic volume are also of basic importance.

In fact, the value of the concept of atomic volume as applied to alloys is seriously to be brought to question. It is well known that the radius of the outermost electron in atoms is much less than the radius of an atom as calculated from the interatomic distances,⁴³ so that it is hardly correct to speak of the physical smoothness of an atom plane. Eventually the whole problem of slip along atomic planes must be put into terms of forces, and in this form the plane of easiest slip is that upon which the interatomic forces normal to the plane are smallest and upon which the distribution of these forces is most symmetrical. A complete theory of mechanical deformation in terms of interatomic forces, however, must await a more complete elucidation of the solid state.

SUMMARY

The importance of the study of interatomic forces in metals and alloys is pointed out. It is shown that data on compressibility and internal pressure furnish a basis for the analysis of the hardness of the pure metals. It is suggested that the electron distribution around the atom periphery probably introduces a slip-resistance factor in addition to that of the crystalline symmetry and the interatomic forces.

The chemical attraction between unlike atoms in certain solid solutions has been approximately evaluated by means of measurements on compressibility and calculations of internal pressure. An analysis of the factors inducing hardness in certain completely isomorphous solid solutions has shown that only a small fraction of the total hardness can be ascribed to the attraction between unlike atoms, but it is pointed out that this attraction is largely contributory in producing slip-resistances of a purely crystallographic nature.

It is suggested that the concept of atomic volume as applied to alloys has certain serious limitations, and that a complete analysis of the factors inhibiting slip should be in terms of force fields.

DISCUSSION

H. W. GILLETT, Washington, D. C. (written discussion).—It is comforting to note from such papers as this, that of Dean and Gregg last year, and many others by various authors in this and other countries, that metallurgists are thinking beyond

⁴³ Sherrer and Debye [*Physik. Zeitschr.* (1918) **19**, 474] state that in the case of carbon the diameter of the outermost revolving electron is only $\frac{1}{4}$ of the interatomic distance. Similar results have been obtained for other elements.

the mechanical analogs or pictures commonly used to describe metallurgical phenomena and are more and more harking back to the atomic forces involved.

Useful as the mechanical key conception of slip-interference is, it lacks something of being a universal explanation for hardening, particularly in the case of solid solutions, and it is of interest to note that Merica, on whose basic interpretation of the phenomena of the hardening of duralumin the slip-interference theory has been built up, himself said⁴⁴ that the added resistance to slip produced by the presence of a key particle is not literally due to the necessity of shearing this particle, but that from the presence of the particle there result additional atomic forces, chemical in nature, acting between the particle and the surrounding layers of atoms.

The force concept appeals to me⁴⁵ as more fundamental than any concept not taking account of forces. The difficulty is to get quantitative data on the forces, since mathematical calculations not based on sound experimental grounds are highly unsatisfying.

Any effort to get quantitative data, such as this work of Dr. Mehl's on compressibility, is praiseworthy and tends to clear up some of the broad outlines of the subject. In view of the difficulty of telling just what the data mean, because of other factors that may come in, it seems wise not to draw too sweeping conclusions from the data. For example, on page 415 it is indicated that the possible error is of the order of 3 per cent., which seems too low a precision to justify the use of the data as very definite proof against the presence of so-called "amorphous metal" in cold-worked metal. I do not believe in the existence of "amorphous metal" in any reasonable sense of the word "amorphous," any more than Dr. Mehl does, but the compressibility data are scarcely adequate to disprove its existence. Similarly in the bearing of the data on the martensite problem, one wonders whether the causes for similar compressibility of annealed and quenched steel varying vastly in hardness may not be somewhat analogous to those for a similar modulus of elasticity, which would hardly be taken as definite proof that the structural units were necessarily identical, since austenitic steels have practically the same modulus as pearlitic steels.

But whether the particular data of this paper can or cannot be used as a basis for sweeping conclusions, honor is due Dr. Mehl for tackling the problem. Everybody is talking about atomic forces, some people are making mathematical computations on them, but very few are attempting to measure them. The more measurements we have, the sooner we will reach the end of the chain, philosophical surmises—mathematical physics—experimental physics—industrial progress based on reliable scientific facts.

H. H. LESTER, Watertown, Mass. (written discussion).—The paper by Dr. Mehl is timely and very pertinent. The progress of human civilization has been and is measured largely by the extension of its control over the inanimate forces of nature. This extension of control, slowly gathering momentum through the ages, has brought us today to epochal development in mechanisms. Mechanisms must depend for their success largely on structural materials which must keep pace in their evolutionary progress with the mechanisms themselves. Bronzes, brasses, steel itself and various types of alloy steels may be said to have been discovered rather than developed. The empirical methods that have characterized very much of past searches for new and better materials were certainly the most economical and possibly the only methods available. The field was large for discovery. But we now approach a period where

⁴⁴ P. D. Merica: Discussion on Slip Interference Theory of Hardening. *Chem. & Met. Eng.* (1922) **26**, 881.

⁴⁵ R. H. Bogue: Theory and Application of Colloidal Behavior, **2**, Chap. 20. 1924. New York, McGraw-Hill Book Co.

further progress must be guided by a more definite and more complete knowledge of the fundamental factors that give metals their physical properties. Dr. Mehl's contribution is directed toward this end.

No doubt the author regards this study as more or less preliminary to an extended search into the effects of atomic forces in their relation to physical properties. Possibly present results will be modified in the light of fuller knowledge. There might be some question, for example, as to compressibility coefficients obtained from cast structures which usually contain microscopic voids due to solidification shrinkage. The hardness measurements are in terms of Brinell impressions which, while perfectly satisfactory for the purposes for which they were intended, involve complicated and not too well understood physical quantities. It would seem that some other method of determining hardness values might be found that would give results more comparable with compressibility ratios. A Brinell impression in a piece of rubber would give the same hardness as it would if made in a diamond (if a diamond could be Brinelled); that is, there would be no impression, neither substance being deformed beyond its yield point. In these cases hardness seems to be purely an elastic phenomenon; the widely differing hardness being perhaps directly comparable to widely differing compressibilities and widely differing atomic forces.

In metals, however, an impression is made which involves, in addition to elastic forces, certain viscosity or frictional resistance forces. While the two types of forces may be regarded as atomic, it seems hardly probable that they vary according to the same law. Brinell hardness measurements are difficult to define in fundamental terms because of the complex nature of this physical property. The relationship between compressibility and metal hardness probably involves a relationship between slip resistance and atomic forces. It would be interesting to trace relationship between modulus values and compressibilities. Perhaps the author plans such comparison for a later communication. Elastic moduli depend directly upon interatomic force. They should be functionally related to compressibilities. It would be interesting to see whether the author's conclusions with regard to the hardness of quenched and annealed steels would be modified by such a study. For instance, there appears to be a somewhat lowered density and slightly lowered modulus in quenched steels as compared with annealed steels. The same seems to be true for cold-worked steels as compared with the same steels before cold work. One would expect lowered modulus to mean increased atomic spacing, which would account also for lowered density. The fact that such changes are not found is significant and probably has some bearing on the distribution of the carbon.

The whole subject of atomic forces and their relation to physical properties seems to be a field ripe for investigation. Dr. Mehl's very interesting and valuable work seems to point to one method of attack. It is hoped that this paper will be followed by others. If the science of metals is to progress far beyond its stage of empirical development, it is necessary that physical characteristics be defined in terms of theoretically sound fundamental concepts.

G. E. DOAN, Bethlehem, Pa.—That the property of pure metals which we call "hardness" is really an expression of the cohesion-pressure caused by molecular attraction has been shown recently by Richard von Dallwitz-Wegner in Heidelberg.⁴⁶ This cohesion-pressure *originates* in the surface phase of the substance, but it acts as an external force on the entire body. It can be calculated according to the equation:

$$K + P = 84.1 \frac{\gamma}{M} \left(t + \frac{1}{\delta} \right) \text{ atm.}$$

⁴⁶ Über Kontakt-Elektrizität, Thermoelektrizität und Kohäsionsdruck. *Zeitschr. für Elektrochem. und angew. physik. Chem* (1928) **34**, 42.

where γ is the density of the metal in kilograms per liter, M is its (chemically relative) molecular weight, $t^\circ \text{C.}$ is the temperature existing, and δ is the cubic coefficient of expansion per degree Centigrade ($\delta = 3\delta'$ where δ' is the linear coefficient as given in the tables). P is the external atmospheric pressure, which may be neglected.

If the metals are tabulated in order of their cohesion-pressures the series is likewise a hardness series with iridium at the hard end, and mercury, lead and tin at the soft end. Diamond (hardness 10 on the customary scale) has a cohesion-pressure of 13,000,000 atm. Then comes quartz (hardness = 6) with four million, etc.

That the force of cohesion acts as an actual external pressure rather than a mere pressure in the surface layer is shown by computing the work done when a body weighing 1 kg. expands on heating 1° against this external pressure. The specific heat is added to the body and one can calculate this specific heat at constant volume,

$C_v \frac{\text{kg. cal.}}{\text{kg.}}$ This will show that the difference of the molecular heats

$$C_{mp} - C_{mv} = R = 1.974 \frac{\text{kg. cal.}}{M. \text{ kg.}}$$

just as is the case with the ideal gases. Furthermore, the ratio $C_{mp}/C_{mv} = 1.6$ as with monatomic gases. It follows from this that the cohesion-pressure in a solid or liquid is really the same thing as an external pressure upon a gas.

For these reasons, the use of cohesion-pressures and compressibility data as adopted by Dr. Mehl seem not only scientifically sound but quite fundamental to the explanation of hardness in pure metals and in solid solutions. Other factors, such as crystal symmetry and subatomic forces, do, no doubt, influence the hardness, as Dr. Mehl points out; but as a fundamental force in determining hardness, that of cohesion-pressure as calculated by the Dallwitz-Wegner equation, or as measured from compressibility data, would seem far more important.

The compressibility measurements on quenched (martensitic) steel and the cohesion-pressure of solid solution such as Ag Au alloys do not, however, explain their superior hardness. They seem to show, rather, that, in the case of alloys, hardness is largely due to some cause other than cohesion-pressure between the atoms or molecules. That martensitic steel should have the same compressibility as pearlitic steel is quite surprising in view of their great difference in hardness. Likewise, the increased hardness of solid solutions over that of the component metals is not accounted for by compressibility. Finally cold-worked copper shows little change of compressibility over annealed copper, although its hardness is enormously increased. In view of the author's results on solid solutions, we may ask the question: "Is the attraction between unlike atoms or molecules always greater than between like atoms?" When the limit of solid solubility between two metals is reached, does that not indicate that the attraction for foreign atoms has been exhausted, even though the space-lattice conditions are favorable as in the silver-copper alloys? Likewise, when two immiscible liquid layers of metal are formed, is that not indicative that the attraction of the atoms within each layer is greater than that for foreign atoms?

At least Dr. Mehl's paper has shown that the increase in hardness of a solid solution over that of the pure components is not satisfactorily accounted for by the increased attraction between unlike atoms or molecules as arrived at by compressibility tests or by calculation of cohesion-pressure. Thus, the rather simple and satisfactory relation between hardness and cohesion-pressure which holds for pure equiaxed substances seems inadequate to account for the increased hardness of solid solutions and conglomerates. It seems, however, to be a thoroughly sound basis from which to start a study of this nature and it is hoped some further light will thereby be thrown upon that very important group of alloys, the solid solutions.

S. L. HOYT, Schenectady, N. Y.—The main point I wish to make in the discussion, aside from commenting on the high quality and great promise of this paper, would be to suggest to the author that he secure better hardness figures. It is unfortunate that an attempt of this kind is really weighted down by such hardness figures as he has. Any metallurgist will appreciate that on going over the hardness figures which are given here.

What I would offer by way of constructive criticism would be that he use the elastic or absolute hardness, for instance, in the Auerbach-Hertz sense; that is, the hardness as measured by a sphere and a plate made out of the same material. That will give him the elastic hardness which conceivably should bear a closer relationship to other elastic phenomena than the Brinell hardness number, which is a purely arbitrary number, with no physical significance aside from what you yourself want to read into it. Even the geometry of the Brinell hardness determination is against it for purposes of that kind. It would be far better if Dr. Mehl would use Meyer's constant a as an indication of the hardness of the material because the constant a bears a much closer relationship to the elastic hardness than the hardness number itself.

So I feel it is to be hoped that Dr. Mehl will continue his work, making use of better measurements of the hardness than he has, and if Dr. Gillett, of the Bureau of Standards were here, I would like to suggest to him that some of the enthusiasm which he himself displays for this work might well be utilized in working on the hardness problem.

J. ALEXANDER, New York, N. Y.—I would like to emphasize several points here. One is that the Brinell hardness seems to be a very variable proposition. If you take the purest obtainable tin and the purest obtainable lead and prepare two specimens of each, one of which has been chilled quickly and the other chilled slowly, the quickly chilled specimen will show about a whole point in Brinell hardness harder than the slowly chilled one. That immediately brings up the point that, entirely apart from these interatomic forces, which undoubtedly exist, we probably are dealing in metals at all times with interfacial forces. Interfacial forces involve the concept of different phases.

Now we may conceive of a substance being dispersed in itself. That is a rather unique conception. I think the first one to bring it out was Wolfgang Ostwald. You may, for example, have finely dispersed ice dispersed in still liquid water. This phenomenon, called isocolloidism, becomes a factor to be reckoned with in the ideal theory which Dr. Mehl has so well brought out in the curves actually obtained. A great deal will depend on what the internal structure of a mass of metals actually is.

Z. JEFFRIES, Cleveland, Ohio.—I want particularly to call attention to one group of facts and its possible relation to this question of internal pressure. Take, for example, a single crystal of copper about $\frac{3}{4}$ in. in diameter. It can be bent at room temperature in the two hands. The resistance to deformation could not be greatly different in point of magnitude even at 1000° C. near the melting point of copper, so that for a long range of temperature in copper the resistance to deformation does not increase very greatly. On the other hand, a single crystal of tungsten at room temperature has a definite elastic limit and may be considered as a relatively hard material as compared with a single crystal of copper. But, on cooling to liquid air, the single crystal of tungsten becomes a really hard substance. The cooling range in the above instance is only 200° C., and the decrease in volume is only 0.33 per cent. This shows that a slight decrease in volume brought about by a change in temperature, if that temperature range is carefully selected, may make a tremendous increase in what we call hardness.

In that particular temperature range, if we should plot a curve of volume decrease against increase in hardness, we would find relations not unlike those shown in Dr. Mehl's Fig. 2.

As a mechanical conception of this phenomenon, last year, some of you may remember, it was pointed out that slip occurs in grooves on the crystal planes and that if the atoms are really physically separated from one another, there could be considerable change in volume without changing the resistance to slip a great deal. But if the atoms become compressed on the plane, either generally or at points so that the planes of atoms can no longer slip smoothly down the grooves but are interfered with by actual contact, you can see at least one mechanism for a tremendous increase in hardness or resistance to slip with a very slight decrease in volume.

We cannot, of course, use the temperature and internal-pressure changes of volume without discretion. Dr. Bridgman has shown, for example, that certain metals which show supraconductivity, when cooled to a temperature near absolute zero, can be compressed at room temperature so that the volumes are less than they would be at absolute zero by calculation, and yet those metals do not exhibit supraconductivity. On the other hand, the relation between volume and cohesion is one which can be used with a greater degree of certainty.

I would like to express my great appreciation for the results reported in this paper and to offer the suggestion that one of the indirect consequences of increase in internal pressure is to bring the atom centers closer together there by interfering with slip.

J. L. GREGG, Chicago, Ill. (written discussion).—I am afraid that, in looking for more than a casual relation between hardness as measured on metals and an elastic constant, such as compressibility, Mr. Mehl has overlooked some fundamental things about "hardness." Hardness as measured by Brinell or scratch process is a measure of the force necessary to produce an irreversible deformation as distinct from the reversible processes involved in compressibility, etc. The discussion of hardness in the first six pages does not, therefore, appear to me to be very useful.

The author quotes Bridgman as finding that severely worked copper and iron gave nearly the same compressibility values as annealed copper and iron. The references given do not seem to indicate so certain a conclusion. The metal that is capable of the greatest work hardening (tungsten) was found by Bridgman to show a distinctly measurable difference in compressibility when in the form of rod and wire, the wire showing the greater compressibility. Taking also Richards' figure for a tungsten pellet, we get the following interesting figures:

Tungsten swaged rod.....	2.93×10^{-7}
Drawn wire.....	3.15×10^{-7}
Fused.....	2.7×10^{-7}

The indications from Bridgman's work are that copper and aluminum show much less, if any, change, but the amount of working is not given in Bridgman's paper and such difference as exists is consistently in the same direction as with tungsten.

It would seem worth while to consider what might be expected from what the metallurgist may fairly say he knows about work hardening; namely, that deformation takes place along certain glide planes and the increased hardness on working results from an interference with the slip along these planes. I do not think that any metallurgist holds today that any appreciable per cent. of the space lattice is fundamentally changed. The thing that is worrying us is the mechanism of this slip-interference and the nature of the space-lattice change immediately around these glide planes. Since the amount of the lattice so changed is small, the change in compressibility would be small in any case. It is unfortunate that the author did not repeat Bridgman's work. That there appears to be a small change in the case of tungsten in the direction of greater compressibility is interesting as indicating that the glide-plane areas have a distinctly higher compressibility. It will be remembered that Beilby found a lower modulus for hardened metal as measured by the note emitted by metal reeds.

Attempts to connect these compressibilities with hardness are quite obviously futile, for reasons previously given. That hardened steel has the same compressibility as the same material quenched is interesting but not "very surprising" in view of the unfortunate fact that the elastic modulus is similarly unaffected in any great degree by hardening.

I cannot agree with the author that data on compressibility and internal pressure furnish a basis for the analysis of the hardness of pure metals, and I wish to emphasize again that hardness as measured metallurgically is resistance to irreversible deformation—compressibility is concerned only with reversible deformation.

R. F. MEHL (written discussion).—The effect on the hardness of duralumin of the interatomic forces operative between the precipitated particles and the surrounding atom layers pointed out by Merica and discussed by Dr. Gillett, should be noticeable, if sufficiently great, in a divergence in the calculated and the observed compressibility coefficients for duralumin. I had planned to investigate this point, but the rapid reaction between the duralumin specimen used and the water serving as a filling medium in the piezometer made the determination impossible. By the choice of a different filling medium, or by the use of another method of measurement, such as Bridgman's change in length method, the determination could be carried out, and might lead to an interesting result.

The accuracy of 3 per cent., to which Dr. Gillett calls attention, refers to the piezometer method of measurement developed by Richards and used here for the determination of the compressibility of alloys. The data quoted on the compressibility of cold-worked metals are Bridgman's, and were obtained by a different method. Bridgman estimates his accuracy to be of the order of 0.1 per cent. I should like to call attention to the fact that the compressibility data taken from Bridgman's work are not quoted as proof against the presence of amorphous metal, but merely as an indication of the absence of amorphous metal in any great quantity (see page 411).

The modulus of elasticity in tension (Young's modulus) cannot be taken alone as unequivocally indicative of the intensity of atomic bonding. In combination with the modulus of elasticity in shear (the modulus of transverse elasticity or of rigidity), however, it can be used to calculate compressibility by the familiar equation, used for the purpose for a number of metals by E. Gruneisen.⁴⁷ A variation in the moduli of elasticity in shear for two substances having identical moduli of elasticity in tension would lead to different compressibility coefficients. (See the fifth paragraph of Mr. Gregg's discussion.) It is therefore a question of which of the moduli should be used as indicative of the intensity of cohesion. Attempts to use these moduli for the purpose were unsuccessful and led to adoption of the compressibility coefficient, the reciprocal of the bulk modulus. This is a constant very little affected by mechanical state and the method for its determination is applicable alike to soft, hard, or brittle materials.⁴⁸

⁴⁷ $\beta = 9C - \frac{3E}{CE} = \frac{3(1 - 2\sigma)}{E}$ where β is the compressibility coefficient, C is the modulus of rigidity, E is Young's modulus, and σ is Poisson's ratio. cf. E. Gruneisen: *Ann. Physik* (1907) **22**, 801; (1908) **25**, 825; also G. Sachs: *Grundbegriffe der Mechanischen Technologie der Metalle*, 9-13, Leipzig, 1925, Akad. Verlag.

⁴⁸ The determinations of the moduli of elasticity in tension and in shear are very difficult for highly plastic materials like lead and for highly brittle materials like the intermetallic compounds, and in addition are vitiated by the presence of small mechanical imperfections, whereas the determination of the compressibility coefficient is relatively very much less sensitive to these conditions. For these reasons a direct determination of the compressibility coefficient is much to be preferred.

A more direct method of estimating the intensity of the interatomic cohesion would be obtained by a determination of the true breaking strength.⁴⁹ In metals, however, this is obscured by mechanical slip⁵⁰ and by the presence of small mechanical imperfections.

The compressibility coefficient is a constant for any given substance. For a mixture, the mean compressibility coefficient may be calculated from the composition by volume; for two mixtures made up of the same components in the same proportions similarity in the compressibility coefficients points to similar structural units, though it does not demand it. This limitation in the significance of the results is implicit in the discussion (page 415, second paragraph). With respect to the main conclusion, that there is no appreciable increase in cohesion accompanying quench-hardening of carbon steels, no qualification appears to be required.

As Dr. Lester points out, the presence of voids in the materials measured would have rendered the results worthless. This error was obviated by the determination of density and a comparison of the determined density with that calculated from the composition. In cases where the determined densities were suspected the alloys were photographed by X-rays. As a result one cast alloy of copper-silicon, which showed a serious shrinkage cavity, was discarded.

Both Dr. Lester's and Dr. Hoyt's remarks on the hardness data used in the paper are quite justified. The object of the present paper was to present new data on the compressibility of alloys for logical analysis from the particular point of view of interatomic cohesion and for examination with respect to their metallurgical significance. It appeared immediately that compressibility and internal pressure had significance for the hardness of metals and alloys. The author was therefore constrained to make use of the hardness data for the pure elements available in the literature, whatever their limitation. That such a course seems justified is fairly evident from the discussion given on page 409.

The recent paper by R. von Dallwitz-Wegner, to which Dr. Doan calls my attention, is very interesting. The equation derived for the cohesion-pressure, though obtained in a different manner, is dimensionally similar to that of Richards. $\frac{\gamma}{M}$ is the reciprocal of the molecular (or atomic) volume, and is identical with $\frac{1}{V_A}$; δ is identical with $\frac{1}{\alpha_s}$; and for a given temperature, t and the factor 84.1 may be compared to R , all of them constants. Cohesion-pressures calculated by this equation for a definite temperature will therefore be equal to those of Richards multiplied by a constant. A tabulation of the cohesion-pressures *versus* hardness will give a series parallel to that of Richards, as Dr. Doan points out.

The first question in Dr. Doan's fifth paragraph is very pointed. It can be answered in only a general way, since direct measurements on the thermodynamic potentials of alloy phases are entirely lacking. Crystallographic factors permitting, two metals will form solid solutions when their mutual attraction is sufficient to overcome the tendency of the metals to occupy their characteristic lattices with characteristic parameters. That is, the average cohesive force (or pressures) in the alloy are greater in the solid solution than the mean of these forces or pressures in the unalloyed metals. The decreases in the compressibility coefficients formed for solid solutions, and the increase in the internal pressures calculated support, so far as they go, this conclusion. With respect to the factors controlling limited solid solubility I should not so much as hazard an opinion. They must include the specific attrac-

⁴⁹ Cf. Sachs: *Op. cit.*, 63-65; also A. Joffe: *Trans. Far. Soc.* (1928) **24**, 65.

⁵⁰ C. H. Desch: *Trans. Far. Soc.* (1928) **24**, 55.

tion factor, together with crystallographic, elastic and electronic factors. Though I have attempted to evaluate these various factors in relation to the known limits of solid solubility for the various systems, I have found no rigorous generalizations.

The discussion by Mr. Gregg seems to miss the essential logical point of the argument given in the paper. The compressibility coefficient is taken, not as equivalent to hardness, but as indicative of the intensity of one of the factors governing resistance to slip, namely, the interatomic forces. Its peculiar virtue lies in the fact that no deformation by slip, no permanent deformation, occurs during its measurement. It therefore isolates one factor in hardness, and gives an estimation of it without reference to those complicated processes which set in when slip occurs. It is therefore complementary to investigations on the mechanism of slip. The value of the argument must rest upon the regularities in behavior it adduces; these are given in various places in the paper, especially on page 409.

The compressibility coefficients for tungsten obtained by Bridgman and quoted by Mr. Gregg are somewhat uncertain in their significance. The material with the higher compressibility (the drawn wire) showed the higher density, a contradictory result. The results on this wire are discussed at some length by Bridgman in the original paper.⁵¹ The compressibility coefficient found by Richards for tungsten pellets, namely, 0.27×10^{-6} , was determined years ago when the method used was in an early stage of development and when high accuracy was not attempted. This is also noted by Bridgman.⁵²

I should again like to call attention to the exact phrasing of the conclusion drawn from Bridgman's results, given in the last sentence in the first paragraph on page 411.

The relation between the elastic moduli and the compressibilities of the steels has been discussed above (in reply to Dr. Gillett). So far as I have been able to determine during an exhaustive search of the literature there has been no determination of the two elastic moduli for annealed and quenched steels. Such a determination would yield information similar to that given here, but would be much more difficult to carry out. A determination of either one of the moduli alone, however, would not be decisive with respect to the cohesive forces present, as previously pointed out.

In concluding this discussion, attention should be called to the recent symposium of the Faraday Society on cohesion,⁵³ in which are discussed a number of problems bearing on those treated here. It is pointed out on page 410 of the present paper that the Brinell hardness for metals of the same lattice type is not strictly paralleled by the internal pressure. It is concluded from this that there are other factors besides the lattice structure and the internal pressure contributing to the resistance to slip, which may include differences in the directional forces operating between atoms, related to differences in electronic distribution in the atom periphery, and which are not revealed by the lattice structure. Additional evidence of the presence of these factors may be drawn from the observation of M. Polanyi⁵⁴ given in the Faraday discussion that though metals of the same lattice type (silver, copper, and aluminum) agree qualitatively in their mechanism of slip, the fiber structures show that the ratio of slip among the various contributing planes is not the same for the different metals.

I should like to express my keen appreciation for the kind discussions of this paper offered by Dr. Gillett, Dr. Lester, Dr. Doan, Dr. Hoyt, Mr. Alexander, Dr. Jeffries, and Mr. Gregg.

⁵¹ *Proc. Am. Acad. Arts & Sci.* (1923) **58**, 168.

⁵² *Op. cit.*

⁵³ *Trans. Far. Soc.* (1928) **24**, 53.

⁵⁴ *Trans. Far. Soc.* (1928) **24**, 77.

Twinning in Copper and Brass*

BY ALBERT J. PHILLIPS,† WATERBURY, CONN.

(New York Meeting, February, 1928)

AS EARLY AS 1824, Haidinger¹ described crystals of native copper that were, according to Dana,² "probably twinned parallel to the octahedral plane and normal to this axis." In 1837, Rose³ very clearly demonstrated that native copper crystals were commonly twinned on the octahedral plane. Lasaulx,⁴ in 1882, described polysynthetic octahedral twins and stated that enclosed twinning lamellae were observed. Even on crystals formed artificially by electrolysis, twinning was observed as early as 1886, by Brown.⁵ Many other descriptions of twinning in native copper and in gold and silver are to be found in the literature, and in every case with which we are acquainted the twinning is conformable to the spinel law; *i. e.*, the octahedral plane is both twinning and composition plane.

Metallurgists have long been familiar with the straight-sided bars or bands that commonly occur within the irregularly outlined grains of metallic crystalline aggregates. They are certainly found in nearly all metals of the face-centered cubic type after cold working and annealing. If a specimen showing these bands is rotated, keeping the angle of incidence of the illuminating beam constant, they usually exchange color contrast periodically with their respective matrix crystals. Also slip lines, when produced in these specimens, nearly always show a change in direction upon passing through the bands, giving rise to the "stairway" effect often illustrated in metallurgical textbooks.

Apparently the only quantitative observations on bands of this sort were made by Osmond and Cartaud⁶ on austenitic steel. They selected,

* Part of a dissertation to be presented by the author to the Faculty of the Graduate School of Yale University in part fulfillment of the requirements for the degree of Doctor of Philosophy.

† Metallurgist, Scovill Mfg. Co.

¹ W. Haidinger: On the Regular Composition of Crystallized Bodies. *Edinb. Jnl. of Sci.* (1826) **1**, 58.

² E. S. Dana: On the Crystallization of Native Copper. *Am. Jnl. of Sci.* (1886) **32**, 413.

³ G. Rose: *Reise nach dem Ural* (1837) **1**, 313, 401; **2**, 453.

⁴ A. Von Lasaulx: *Sitzungsber, Niederrhein, Ges.* Bonn, July 3, 1882.

⁵ W. G. Brown: Crystallographic Notes on Artificial Copper Crystals. *Am. Jnl. of Sci.* (1886) **32**, 377.

⁶ F. Osmond and G. Cartaud: The Crystallography of Iron. *Jnl. Iron Steel Inst.* (1906) **3**, 444.

from an aggregate of austenite crystals, one containing a set of cubic planes parallel to the polished surface. By carefully cutting a cross-section through the crystal at right angles to the surface, along a predetermined line, a cubic plane belonging to another set was exposed. They were then able to demonstrate that the two pairs of twin bands which could be seen on these exposed cubic surfaces were parallel to octahedral planes.

This somewhat scanty evidence, coupled with the knowledge that octahedral twins are common in natural metallic crystals, has constituted, so far as I can ascertain, the best justification for the almost universal judgment that these bands are caused by twinning along octahedral planes.

Tammann and Meyer⁷ have recently contradicted this assumption. After determining orientations in cold-rolled and annealed copper by their method of "maximum glitter" (*maximale Schimmer*), they stated that, "In recrystallized copper the twinning plane is not the octahedral but the icositetrahedral (trapezohedral) plane." Since they employed a new and seemingly unproved method admittedly incapable of indicating the exact orientation of a crystal, their conclusion can be accepted only provisionally. Even more recently, Dr. C. F. Elam⁸ reported the occurrence of banded structures in aluminum and in native copper, which, when examined by means of X-rays, did not give evidence of a twin relationship to the rest of the crystal.

INVESTIGATION OF BANDS IN COPPER AND ALPHA BRASS

In view of these discrepancies the following work was done in an attempt to definitely settle the character of the familiar bands in recrystallized copper and alpha brass.

Since the stereographic projection probably offers the best general method of plotting planes in space, it has been chosen as a medium for expressing the results of the present investigation. While this method is constantly used by crystallographers, it has been so infrequently adopted by metallurgists in general that the following rather detailed description seems appropriate.

To fix a plane in space, it is necessary to know only the location of two lines in that plane. For example, in Fig. 1, if oa represents the intersection of an unknown plane with the horizontal plane marked "top" and oa' , its intersection with the front vertical plane, then by means of the angles which these lines makes with vw , the intersection of the vertical and horizontal planes, the unknown plane can be located. This is done stereographically in Fig. 2, where the equatorial plane of the projection coincides with the horizontal plane and the diameter marked "edge"

⁷ G. Tammann and H. H. Meyer: Die Änderung der Kristallitenorientierung bei der Rekristallisation von Kupfer. *Zeitschr. für Metall.* (1926) **18**, 176.

⁸ C. F. Elam: Banded Structure in Aluminum. *Nature* (1927) **120**, 259.

represents the trace of the front vertical plane. The horizontal angle woa in Fig. 1 is represented by the angle woa in the projection, while the

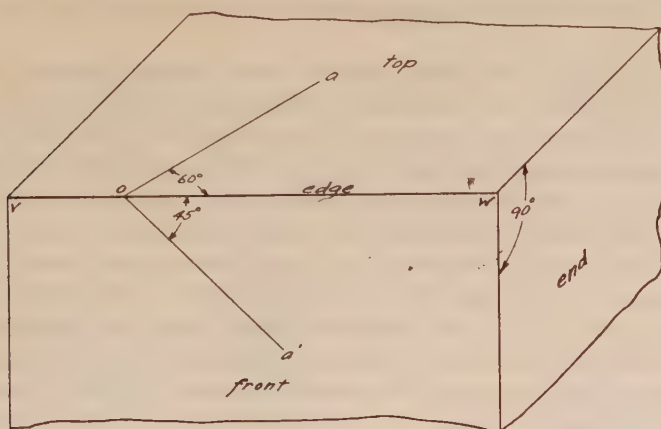


FIG. 1.—TRACES OF AN UNKNOWN PLANE ON A HORIZONTAL AND VERTICAL PLANE.

vertical angle woa' is represented by the angular distance wa' . The arc $usa'a$ is the stereographic projection of the semicircle in which the unknown plane cuts the sphere of reference. By a convention which

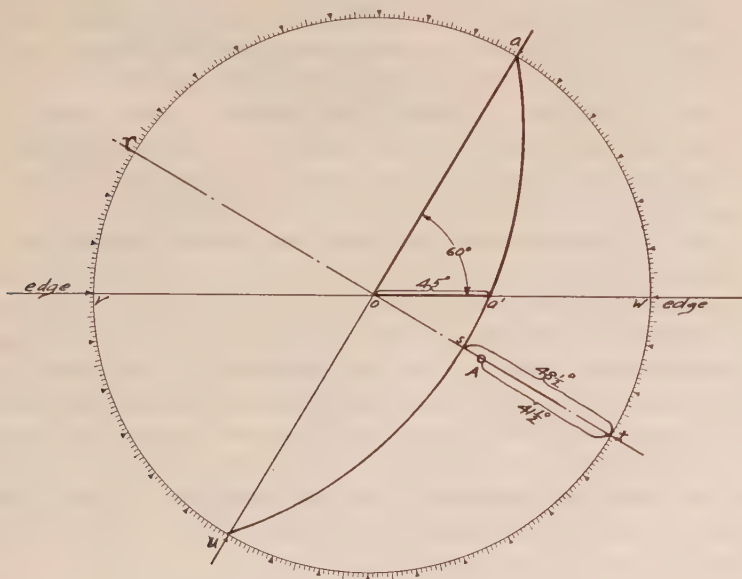


FIG. 2.—STEREOGRAPHIC PROJECTION OF FIG. 1.

permits representing both hemispheres within the divided circle, the pole of this plane is shown by point A , located at 90° from point s along the vertical great circle rt . It should be noted that the convention has been

adopted of drawing constructions in the lower hemisphere with the point of sight at the top of the sphere while the poles of planes are presented in the upper hemisphere by transferring the point of sight to the bottom of the sphere.

If another unknown plane were to pass through the same horizontal and vertical planes, it could also be plotted on the projection and the angle that it would make with the first unknown plane could be determined by measuring the angular distance between their two poles. This may be done in the conventional manner by first determining the great circle on which the two points lie and then the angular distance between these points, by constructing the appropriate small vertical circles. Stereographic nets, described by Wulff,⁹ are most convenient for these determinations. If the two unknown planes are similar crystallographically, the angle between them may be unique and permit recognition of their form. For example, the distance between all cubic planes is 90° ; between octahedral planes $70^\circ 31' 44''$; between dodecahedral planes, 90° or 60° , etc.

From the foregoing it is apparent that if a sample of metal containing banded coarse grains is polished on two surfaces at 90° ¹⁰ to each other, in such a manner that two or more sets of bands can be traced on each surface of a single crystal, the planes which these bands occupy can be determined and, in all probability, recognized from their dihedral angles.

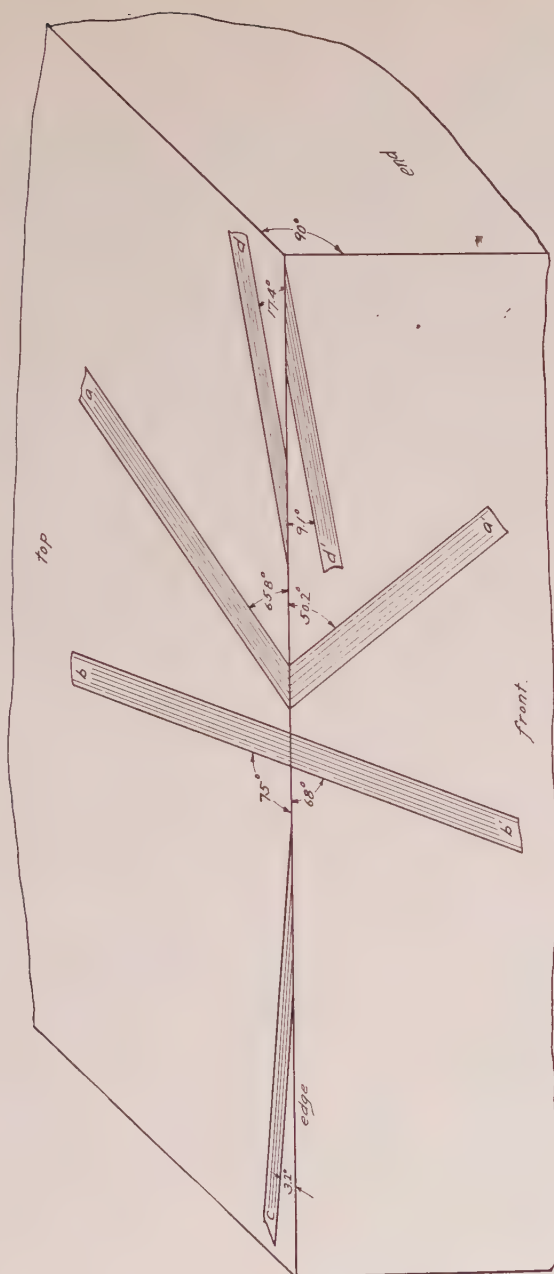
To test this, specimens of deoxidized copper were prepared by stretching a strip of annealed cold-rolled material 2 per cent. and then reannealing at 950°C . for 12 hr. to produce coarse grains. Several pieces 1 by $\frac{3}{16}$ by $\frac{1}{2}$ in. were cut from the central section of the strip and prepared for microscopic examination on two surfaces at right angles to each other, taking pains to preserve a sharp edge at their intersection.

Several of these specimens contained one or more crystals with bands in a suitable position for measurement. The sketch, Fig. 3, shows the angles between the bands and the edge on both surfaces of such a crystal, while the circles in Fig. 4 show the stereographic location of the poles of the corresponding planes. The square marked [001] was found to represent the best location of the cubic axis and thus indicates the orientation of the crystal, while four crosses mark possible locations of octahedral planes around this axis. Their agreement with the three points determined from actual measurements is quite satisfactory. It should be noted that bands *a* and *b* only (Fig. 3) could be traced over the edge from the horizontal into the vertical plane.¹¹

⁹ G. Wulff: *Zeitschr. für Krystall.* (1902) **36**, 14.

¹⁰ The angle of 90° is adopted merely for convenience. Any other known angle would suffice.

¹¹ The position of the cubic axis is, in fact, fixed by two associated pairs of bands; additional data merely confirm the conclusion.



Copper 135C1.

FIG. 3.—POSITION OF TWIN BANDS IN A COPPER CRYSTAL.

When the measurements were made it was not recognized that the traces d and d' could be explained by octahedral planes of the same set. Upon proceeding with the construction, however, this became apparent. Since the band c was found only on one surface, the position of its pole could not be located but its observed trace in the horizontal plane fixed the location of the vertical great circle which includes its pole and is shown in the projection as the diameter C . Here also the theoretical position of an octahedral plane falls quite close to the determined line.

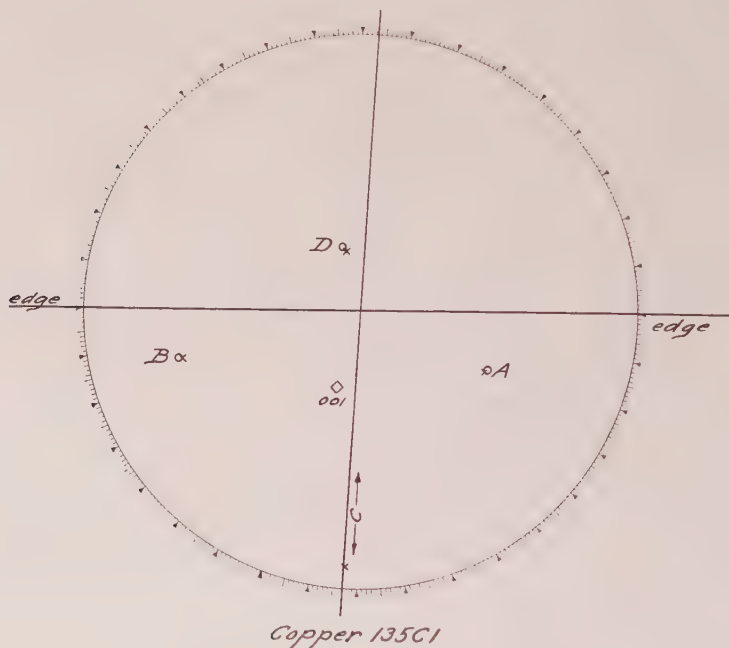


FIG. 4.—STEREOGRAPHIC PROJECTION OF FIG. 3.

Measurements and projections similar to those just described were made in the case of three copper and eight brass crystals. In every case all the bands observed were found to fit the assumption that they occupied octahedral planes. While this is very strong evidence that bands are caused by twinning along these planes, it is not positive proof, since no attention has been paid to the crystallographic orientation of the material within the bands. For example, in case of spinel twinning, an axis of fourfold symmetry in a twin should lie at $70^{\circ} 31' 44''$ to a similar axis in the untwinned portion. If some such orderly relation within the bands measured does not prevail, we are not dealing with true twinning in the accepted sense.

It was observed early in the course of this work that many of the large bands measured contained internal small bands as illustrated in Figs. 5 and 6. These small bands appear to be related to the bands containing them in exactly the same way as the latter are related to the main

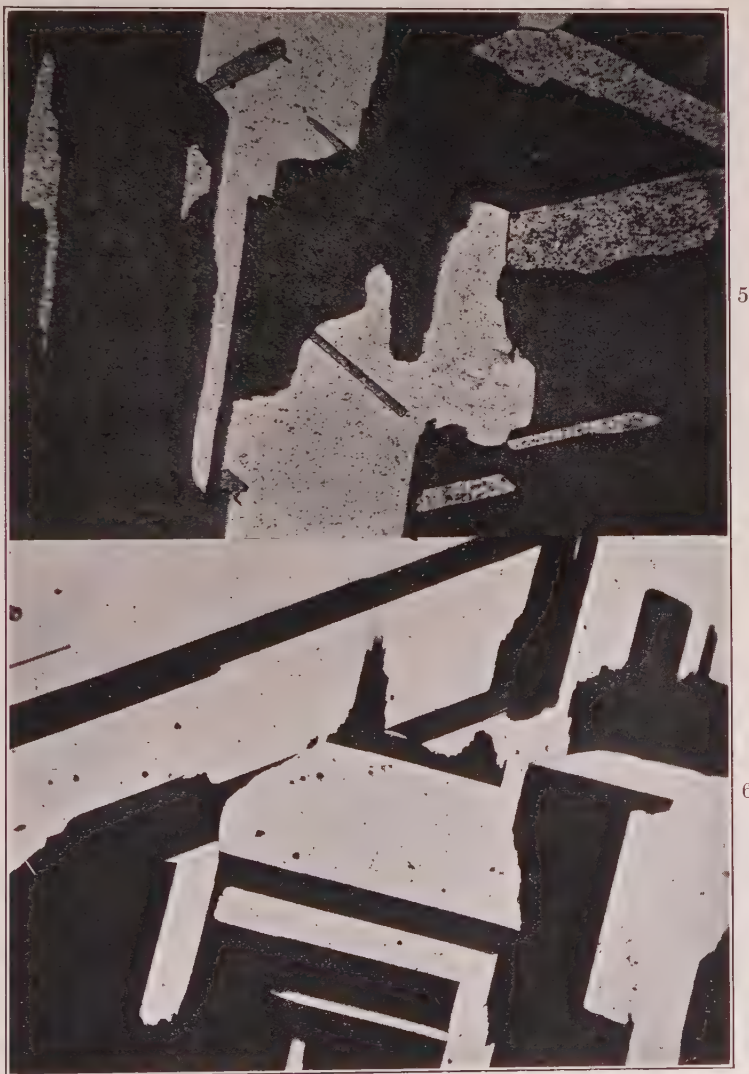


FIG. 5.—TWIN BANDS IN A SINGLE CRYSTAL OF COPPER.
FIG. 6.—TWIN BANDS IN A SINGLE CRYSTAL OF BRASS.

crystal. Granting the assumption that all the bands are twins along octahedral planes, the small bands must occupy positions that can be exactly calculated from measurements like those previously described. It is, perhaps, necessary to caution the reader that the small bands are

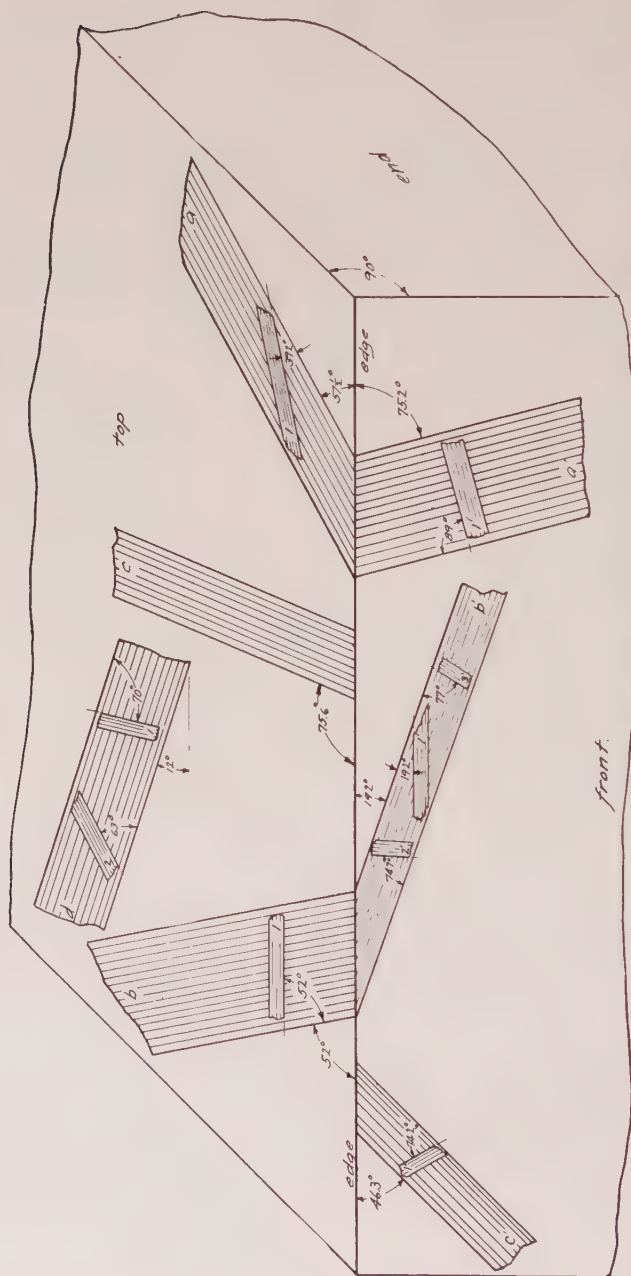


FIG. 7.—POSITION OF TWIN BANDS AND THEIR INTERNAL TWINS IN A CRYSTAL OF BRASS.

not directly related to the main crystal, in spite of the fact that their enveloping band is twinned with respect to it.

Fig. 7 is a sketch of two surfaces of a brass crystal, giving the location of the main bands and their internal twins. A stereographic representation of these data, using the horizontal or "top" surface as the plane of the projection, is given in Fig. 8. Here, as in Fig. 4, the circles at *A*, *B* and *C* represent the poles corresponding to the bands *aa'*, *bb'* and *cc'*, while the pole representing the fourth band must lie on the diameter *DD*. The agreement of the observed data with the theoretical locations of the octahedral planes (indicated by crosses) is quite close.

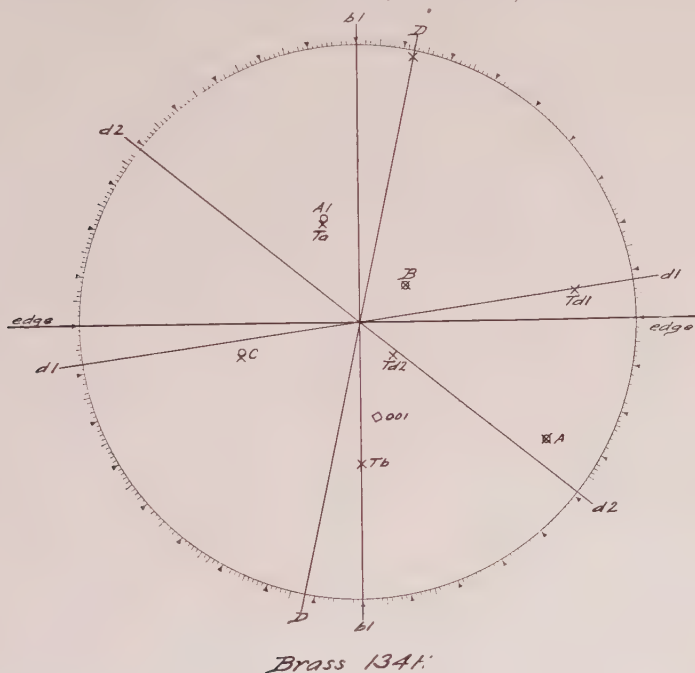


FIG. 8.—STEREOGRAPHIC PROJECTION OF FIG. 7. CONSTRUCTED ON THE HORIZONTAL PLANE.

Within the band *aa'* an internal band was observed on the horizontal surface and another on the vertical surface. If it is assumed that these are traces of the same plane, its pole is given by the circle *A1* in the projection. The cross *Ta* represents the theoretical position of one of the octahedral planes within the twin band *aa'* and agrees quite closely with the determined point.

Twin band *bb'* shows one internal band on the horizontal plane and three on the vertical. Since the band marked 1 is obviously parallel to the intersection of the vertical and horizontal planes, its pole cannot be exactly located but must lie along the diameter *b1*, *b1*. Here again the cross *Tb* marks the theoretical position of an octahedral plane within the

band bb' and falls directly upon the determined line. The other two bands of bb' , as well as the only band in cc' , having been observed on the vertical plane, cannot be conveniently located in Fig. 8.

The poles of the two internal bands of twin d must lie along the diameters $d1, d1$ and $d2, d2$ and are undoubtedly exactly located by the two theoretical points marked $td1$ and $td2$.

Fig. 9, like Fig. 8, is a stereographic projection of the crystal sketched in Fig. 7, but the plane of the projection in this case is the vertical or front face. It was constructed to make sure that the internal bands which

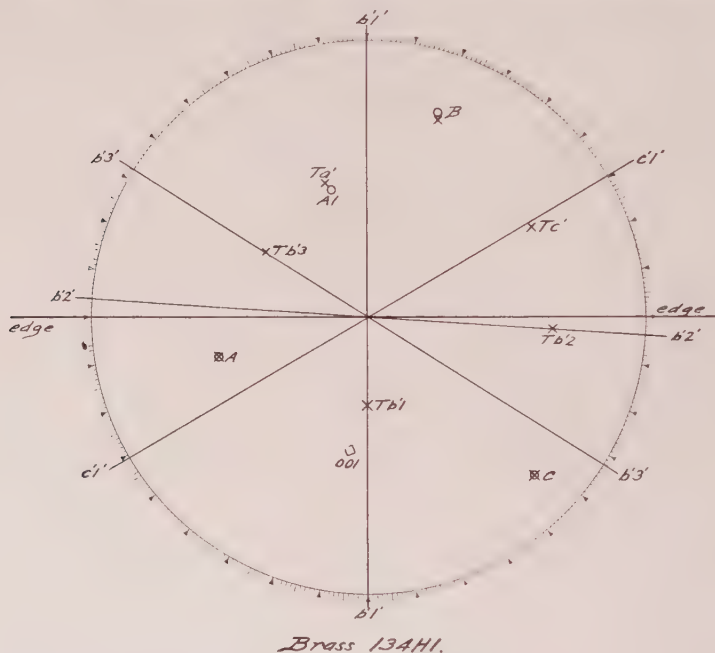


FIG. 9.—STEREOGRAPHIC PROJECTION OF FIG. 7. CONSTRUCTED ON THE VERTICAL PLANE.

are not shown in Fig. 8 occupy rational twinning positions. That such is indeed the case is readily evidenced by the close coincidence of the theoretical poles $Tb'1$, $Tb'2$, $Tb'3$ and Tc' with the lines $b'1'$, $b'2'$, $b'3'$ and $c'1'$ deduced from the measurements.

The foregoing affords convincing proof that the bands commonly encountered in copper and brass are twins of the spinel type. It further suggests that bands of similar appearance in other metals of the face-centered cubic lattice are due to twinning according to the same law.

ACKNOWLEDGMENT

The research outlined in this paper was carried out at Hammond Laboratory, Yale University, under the direction of Prof. C. H. Mathewson, to whom the author is greatly indebted.

DISCUSSION

N. B. PILLING, Bayonne, N. J. (written discussion).—Mr. Phillips has twitted us gently for having made too tacit an assumption about the nature of the familiar banded structures in copper and many copper alloys, and has then proved very obligingly that the guess was right after all. Several years ago an example of this structure

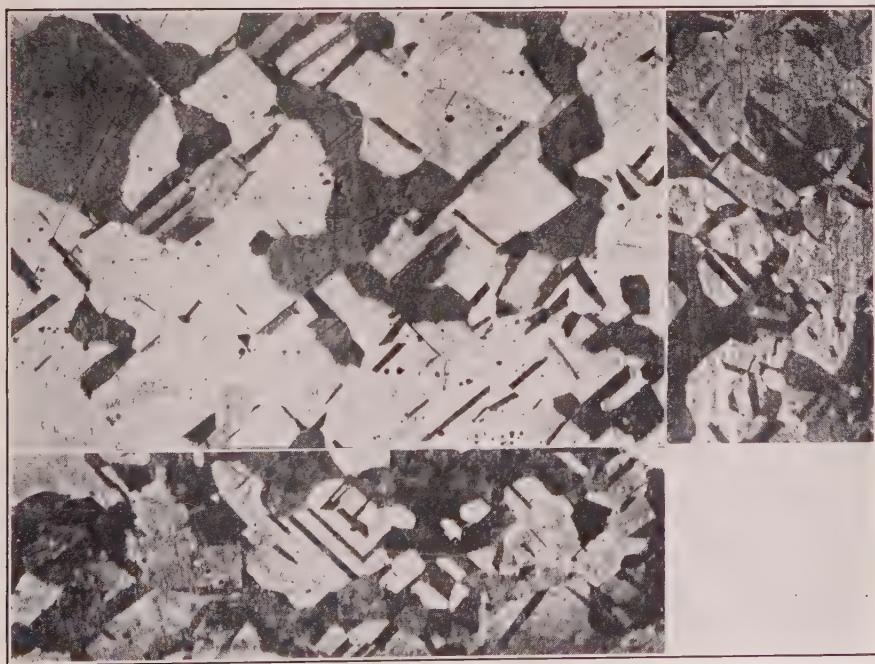
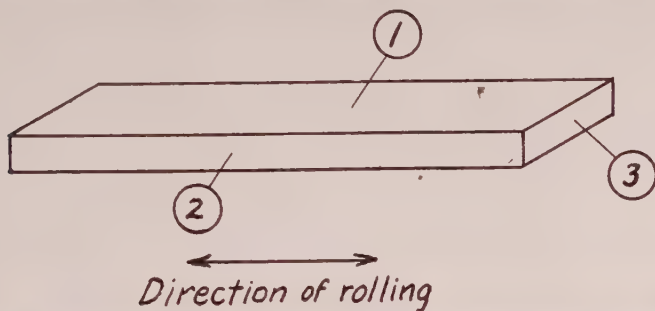


FIG. 10.—LIGHT ETCHING GRAINS HAVE CUBIC AXES PARALLEL TO MAJOR AXES OF ROLLED STRIP, AND TWIN BANDS SHOW AS TRACES OF OCTAHEDRAL PLANES. $\times 100$.

in annealed copper came to my attention, which had so many unusual features, including a direct demonstration of the position of these bands with respect to the lattice, in agreement with the proof Mr. Phillips has just given, that it may be of some interest in this connection today.

The specimen was taken from an electrolytic copper wire bar having the analysis: Cu, 99.94 per cent.; O, 0.066; Fe, 0.003; S, 0.002; Pb, nil; Sn, nil. This bar had

been hot rolled to a thickness of 0.27 in. annealed and then cold rolled to strip 0.043 in. thick, a reduction in thickness of 84 per cent. After annealing an hour at 900° C. a microsection in the plane of rolling revealed the structure shown by Fig. 10. The unusual feature of this lies in the fact that although it is not a single crystal, the "twin bands" of the aggregate are closely parallel to two principal directions at right angles to each other and both inclined 45° to the long dimension of the rolled strip, which was parallel to the bottom edge of the slide.

The geometry of this arrangement is more clearly shown in this model in which the microstructures of random surfaces in three planes mutually at right angles to each other and parallel to the length, breadth and thickness of the rolled strip are given. The twin bands maintain the same relative position in all three planes and it is necessary to make only one assumption—that copper crystallizes in some cubic lattice—to see at once by inspection that:

1. Most of the grains lie in a nearly common orientation in which the cubic axes of the lattice are parallel to the length, breadth and thickness of the rolled strip;
2. The twin bands within these grains truncate the cube corners of the lattice equiangularly and therefore must be bounded by octahedral planes.

A close study of these photomicrographs will show other interesting features which will not be discussed, not being directly related to the subject of Mr. Phillips' paper.

It may be noted that portions of this same rolled strip annealed at considerably lower temperatures showed an entirely random grain orientation and that other portions of the same copper cold rolled less drastically failed to develop a preferred orientation on annealing at any temperature. The present effect was not a chance happening, but was repeated several times.

L. W. MCKEEHAN, New Haven, Conn.—We have here a good deal of experimental work expressed in a very simple and adequate form. In metals which have the same crystal structures, conditions which cause or prevent twinning are frequently very different. The authors have noted in connection with the paper on beryllium, magnesium, zinc and cadmium¹² that the ease of producing twins in beryllium, magnesium and cadmium is different from the ease of producing twins in zinc. The crystallographic structures in the case of these three metals are quite similar except that there are differences in the axial ratio. We are compelled to consider the crystal structure as giving only a small part of the properties of the metallic crystals. Perhaps too much has been said in the past about the fact that the face-centered cubic structure characteristic of copper is a close packing of spheres. If the things which are packed are very nearly spheres, a twin boundary, a composition plane between twins, has no more irregularity of atomic forces in it—of course, between adjacent atoms—than has a corresponding plane anywhere in one solid crystal; but if the things that are packed are very different in their symmetry from spheres, a composition plane between twins may be a region of severe strain and in such metals preservation of twins would be more difficult.

In this sort of work, as well as in the study of forces necessary to produce slip along these planes and others, we may hope to get a great amount of information regarding the actual interatomic forces which formed the subject of an earlier paper this morning.¹³

C. F. ELAM, London, England (written discussion).—Mr. Phillips' paper shows that, in the samples of copper and brass measured by him, the twin bands appear to make angles of approximately 70° with each other. This is the angle between octahedral planes of a cubic crystal, but other planes in the cubic system have this value for their dihedral angle; *e. g.*, certain planes of indices {112} are 70° apart. The whole problem depends on the correct determination of the crystal axes, and there is nothing

¹² See page 445.

¹³ See page 405.

in the present paper to show that this was done. The only reference is on page 432, where it is stated that "the square marked [001] was found to be the best location of the cubic axis and thus indicates the orientation of the crystal." Perhaps the author has some information that does not appear in the paper, but in any case the determination of one axis, even in the cubic system, does not fix the position of all the planes. If this point was determined on the assumption that the bands followed the traces of octahedral planes, the author was assuming what it was desired to prove, and any conclusions arrived at are valueless. Further, it is not justifiable to make determinations on the inclinations of planes, unless the traces on both sides of the specimen can actually be shown to belong to the same plane.

If the author can complete his measurements as indicated, it will very much strengthen his supposition that the familiar banding in copper and brass is of the same nature as the spinel twin.

A. C. LANE, Tufts College, Mass. (written discussion).—In the second volume of the *Bulletin* of the Geological Survey of America (1891, p. 368) using the same stereographic methods as Phillips, I solved the problem of the locus of all sections in which the trace of a known solid angle made a given angle. It is a biquadratic, and if two such angles were given only certain sections were possible. If this locus were computed for the octahedral faces, and for various values of the angle as seen in section, as I did for pyroxenes in my Fig. 6, it would be a simple matter to identify lines such as Phillips describes. Whether the problem occurs frequently enough to be worth while, I do not know.

I found that little irregularities in straight-line twin boundaries were much more marked when the angle to the plane of section was small, and certain features in Phillips' excellent photographs lead me to wonder if it may not also be true in his surfaces.

C. BENEDICKS, Stockholm, Sweden (written discussion).—The method used by Mr. Phillips—that of measuring the plane angles, formed on two ground surfaces (inclined 90° or any other known angle) by the intersecting unknown planes, and then constructing the stereographic projection—evidently is entirely correct. It has, however, the inconvenience of being rather laborious, and applicable only for comparatively large unigrain specimens.

The writer for a long time has used another method, which may be found to be more convenient at least in some cases. This method permits of deciding whether the angles seen in any photomicrograph correspond to intersections given by the three hexahedral planes, four octahedral planes, six dodecahedron planes, and so on, and evaluating, with the accuracy of some degrees, the orientation of the polished surface in relation to these crystallographic planes.

No description of this method has been published hitherto. It is founded on the preliminary construction, on transparent cloth, of a kind of angular protractor (or abacus) drawn systematically so as to evidence essentially all the possible angular directions, produced say by the four octahedral planes, on any plane (polished) surface. This preliminary work does not involve so much labor as might be supposed. As a matter of fact, on account of the symmetry of the isometric system, all possible angular configurations which are obtained on a polished surface (the stereographic pole of which is X) from the octahedral planes are obtained, if X is allowed to occupy varying positions inside an area on the stereographic projection, which is limited by four great circles: two of them passing through the poles (100) and (001) (a straight line when, as generally, the pole of (001) coincides with the center) and through (100) and (111) respectively, the other two passing through (010) and (001) (a straight line) and through (010) and (111) respectively.

The arbitrary position of X inside this elementary area may be obtained from two variables α and β , α being the angle between the great circle $(010) \times (010)$ and the great circle $(010) (001) (010)$, and β that between the great circle $(100) \times (100)$ and $(100) (001) (\bar{1}00)$.

Further, allotting to α , say, the six values $0^\circ, 9^\circ, 18^\circ, 27^\circ, 36^\circ$ and 45° , and likewise to β , 36 X -points are obtained regularly distributed in the elementary area. Constructing then the angular configurations for these 36 points, which may be made by calculation or, more conveniently, by a graphical method—only 21 are necessary to evaluate, the other being merely mirror images—a synopsis is obtained, showing every type of angular configuration formed on a polished surface X by the intersection of the octahedron planes.

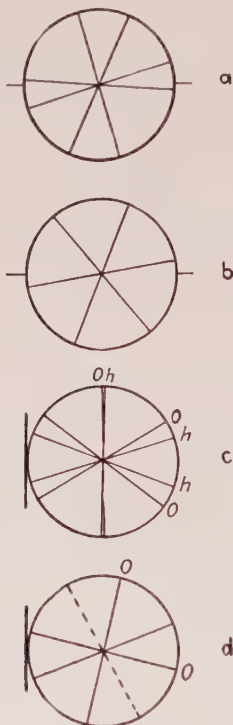


FIG. 11.

As an illustration of the use of this method, the angular measurement on the top surface of the specimen Fig. 3 are reproduced in the angular characteristic Fig. 11a. Examining this with the protractor (or abacus) just described, as constructed for the octahedral surfaces, it is found to come rather near to the characteristic for $\alpha = 27^\circ, \beta = 18^\circ$ and also to that for $\alpha = 36^\circ, \beta = 18^\circ$; hence by interpolation the polished surface may be considered to correspond approximately to the point X_1 given by $\alpha = 30^\circ$ and $\beta = 18^\circ$ (or by a point similarly situated in any of the similar neighboring elementary areas).

Further, the angular characteristic Fig. 11b is obtained for the front surface of Fig. 3. This is found to correspond to a point X_2 given by $\alpha = 45^\circ, \beta = \text{about } 42^\circ$; the presence of three intersection lines only is peculiar for all polished surfaces (X) situated in the zones $(111) (110)$.

Transporting the X_1 value into an adjacent elementary area, and measuring its angular distance to X_2 (using the stereographic protractor designed by S. L. Penfield), an angle of about 89° is obtained.

In a similar way, the twin bands on the top surface of Fig. 7 are found to correspond quite closely to octahedron surfaces ($\alpha = 9^\circ$, $\beta = 36^\circ$); the internal twins, or triplets, similarly correspond to octahedral surfaces of a crystal in a twinned position.

Thus, within the precision of these measurements, the results so far obtained are in a very satisfactory accord with the results obtained in the paper, in a more elaborate way.

Further, drawing the angular characteristic of the photomicrograph Fig. 5 for copper, Fig. 11c is obtained. This angular configuration seems scarcely obtainable from primary octahedral surfaces only. As a matter of fact, the three directions marked O do coincide with octahedral planes (X being a point $\alpha = 45^\circ$, $\beta = 27^\circ$). On the contrary, the directions marked h differ decidedly from any possible section given by the primary octahedron. They actually coincide rather closely with the sections of the corresponding hexahedron, as was established by the use of a similar protractor, constructed for the hexahedral surfaces. This question, however, was not thoroughly analyzed; it does not seem excluded that the two directions h , h may not belong also to a secondary twin.

The angular characteristic of the other photomicrograph Fig. 6, for brass, is reproduced in Fig. 11d. The three or four directions in this case are not obtainable as sections given by a single octahedron crystal. The only coincidences to be obtained with the protractor are for the diameters marked O , which are at right angles corresponding to $\alpha = 0^\circ$, $\beta = 0^\circ$ (*i. e.* X belonging to a hexahedric surface). The other directions seem to correspond rather well—no actual construction being made—to secondary twins. These probably may be considered as twins of an adjacent grain, occupying itself a twin position to the first.

This short analysis lends support to the conclusion drawn by the authors.

The essential problem still to be more closely examined seems to be the question regarding the mutual orientation of the crystal grains. It seems probable, from the foregoing, that some adjacent grains in annealed copper or brass may be orientated according to the octahedral twinning rule, and it does scarcely appear excluded, that most grains remaining after a prolonged annealing may be orientated in this way.

A. J. PHILLIPS (written discussion).—Mr. Pilling has called attention to a very interesting method of developing preferred orientations in copper. While I believe that a complete understanding of phenomena such as this is of great importance, at the present time our fundamental knowledge of the deformational and annealing characteristics of even simply stressed single crystals is so far from complete that one can do little more than guess at the explanations of these more involved cases.

Professor McKeehan's thoughtful suggestion regarding interatomic forces merits the special attention of students of atom structure. A brief study of the atomic adjustments that must take place during twinning makes it apparent that the effective field of force of an atom is not of equal intensity in all directions.

Dr. Elam has called attention to the fact that certain pairs of trapezohedral planes are separated by an angle of 70.5° . She has neglected to note that with any particular trapezohedral plane there is only one other similar plane that makes this angle. My measurements show that with any particular twin band all the other twin bands (as many as three) make dihedral angles of 70.5° , a condition that is unique for octahedral planes. The cubic axis marked $[001]$ in Fig. 6 was determined from the locations of the various twin markings and I can see no objection to this procedure since it was demonstrated prior to locating the cubic axis that the markings occupied octahedral planes. I believe that the following is the only tacit assumption made: if, in a simple

crystal lattice, four similar planes are so located that all possible dihedral angles between them have the value of $70^{\circ} 31' 44''$ (or its supplement) they are octahedral planes. The whole science of crystallography was dependent on this and similar assumptions prior to the discovery that X-rays could be used to determine crystal lattices.

Dr. Elam condemns the correlating of twin-band markings on two surfaces unless they have been matched up by actual observation. It should be noted that in all of our experiments at least two sets of twin bands were matched up by tracing them from one prepared surface on to the other. However, if all unassociated traces lying in the two prepared surfaces are always found to lie in planes bearing an octahedral relationship to the two precisely determined planes, it seems justifiable to associate those pairs of traces which, taken together, will definitely locate an octahedral plane.

When this work was started a mathematical solution of the problem, such as suggested by Professor Lane, was attempted. A formula was deduced before it was realized that the peculiar angular configuration of any associated set of markings may be afforded in many cases by two or more different orientations. Of course, it is not necessary to determine orientations to prove that twin bands occupy octahedral planes but, to prove the twinning law by an analysis of the location of "internal twin bands," it *was* found necessary to know the orientation of the prevailing crystal.

Professor Benedicks' surprisingly simple method of attacking the problem is practically the same as that suggested by Professor Lane except that it is graphical instead of mathematical. It should be noticed that this method, like the mathematical one, does not determine orientations and, as a result, it fails when applied to the analysis of "internal twin bands."

With his usual acumen, Professor Benedicks has pointed out that the appearance of second-generation twin bands upon annealing indicates "that some adjacent grains . . . may be orientated according to the octahedral twinning law . . ." In the near future we hope to offer a demonstration that very many of the crystals, in those metals which commonly twin, bear a computable relationship to one another through multiple internal twinning.

Twinning in Beryllium, Magnesium, Zinc and Cadmium*

By C. H. MATHEWSON,† NEW HAVEN, CONN., AND A. J. PHILLIPS,‡
WATERBURY, CONN. ¶

(New York Meeting, February, 1928)

BERYLLIUM, magnesium, zinc and cadmium, together with mercury, constitute a coherent sub-group of the periodic system and these metals, excepting mercury, have been studied in sufficient detail by the new X-ray diffraction methods to prove their common adherence to the hexagonal close-packed type of crystal structure with a progressive increase in axial ratio as we pass through the group from beryllium to cadmium. The first four columns of Table 1 summarize the data on crystal structure of these metals reported in the International Critical Tables.¹ The last two columns are based on results obtained in the present investigation.

TABLE 1.—*Lattice Constants and Twinning Law of the Be-Cd Group of Hexagonal Metals*

Element	Dimensions of Unit Cell, Å		Axial Ratio	Description of Twinning	
	a°	c°	(c°/a°)	Composition Plane	Axis
Beryllium.....	2.28 ₍₃₎	3.60 ₍₇₎	1.58	{10 $\bar{1}$ 2}	} Probably \perp {1012} \perp {10 $\bar{1}$ 2} Probably \perp {10 $\bar{1}$ 2}
Magnesium.....	3.22	5.23	1.62 ₍₄₎	{10 $\bar{1}$ 2}	
Zinc.....	2.65 ₍₇₎	4.94 ₍₈₎	1.86 ₍₂₎	{10 $\bar{1}$ 2}	
Cadmium.....	2.98	5.63	1.88 ₍₉₎	{10 $\bar{1}$ 2}	

Twinning has often been observed in zinc and cadmium. The general aspects of this twinning are abundantly illustrated by photomicrographs, diagrams, etc., in the papers by Romig, and Mathewson and Phillips reported to this Institute in 1927.² A determination of the composition

* From a part of a dissertation to be presented by A. J. Phillips to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Professor of Metallurgy, Yale University.

‡ Metallurgist, Scovill Mfg. Co.

¹ *International Critical Tables*, 1st Ed., 340-341 (1926).

² O. E. Romig: Preparation of Metallic Single Crystals and Twinning in Zinc and Zinc Single Crystals. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 90; C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Ibid.*, 143.

plane and twinning axis by crystallographic observations on large single crystals was given in the paper by Mathewson and Phillips. Twinning was found to occur in a true crystallographic sense along planes of form $\{1012\}$. This was confirmed by X-ray measurements made by McKeehan and Bozorth and reported in an appendix to the above paper.³

Although axial ratios of beryllium, magnesium and cadmium have been reported in the literature of crystallography⁴ (in very close agreement with the newer X-ray results in the first two cases, but quite at variance with these results in the latter case), we can find no record that a twinning law has been determined in the case of any of these metals.

TWIN BANDS IN DEFORMED METALS

For this reason and in view of the important bearing of crystallographic twinning upon the processes of plastic deformation and recrystallization, we have made a careful examination of the twin lamellae which appear in these metals when they are deformed.

Some preliminary experiments with cadmium convinced us that we could not readily obtain large single crystals by the method of straining and annealing previously used in the case of zinc. Anticipating further difficulties with beryllium and magnesium, we decided to rely upon such crystals as could be obtained in the cast form by slow cooling.

Preparations obtained in this manner were cut so as to expose two surfaces at right angles to one another and searched for crystals simultaneously appearing on both surfaces. When a number of suitable crystals were found the samples were slightly deformed by pressure and then repolished in an attempt to produce a number of twin bands in a given crystal which could be clearly traced across the edge from one exposed surface to the other. Naturally, several attempts had to be made before a sufficient number of properly located twin bands were made available for angular measurements under the microscope. In this connection, we found that twin lamellae produced by pressure between the jaws of a vise vary considerably in size and number, depending on the purity of the metal. Small and closely intermeshed lamellae were plentifully formed in the soft pure metals close to the point of application of the stress. In order to distribute the stress more uniformly through the body of the metal, thereby causing relatively large lamellae to appear, it was often necessary to stiffen the metal by alloying. Thus we used in the final experiments a sample of beryllium containing $\frac{1}{2}$ per cent. of iron as received from the Beryllium Corporation of America, magnesium to

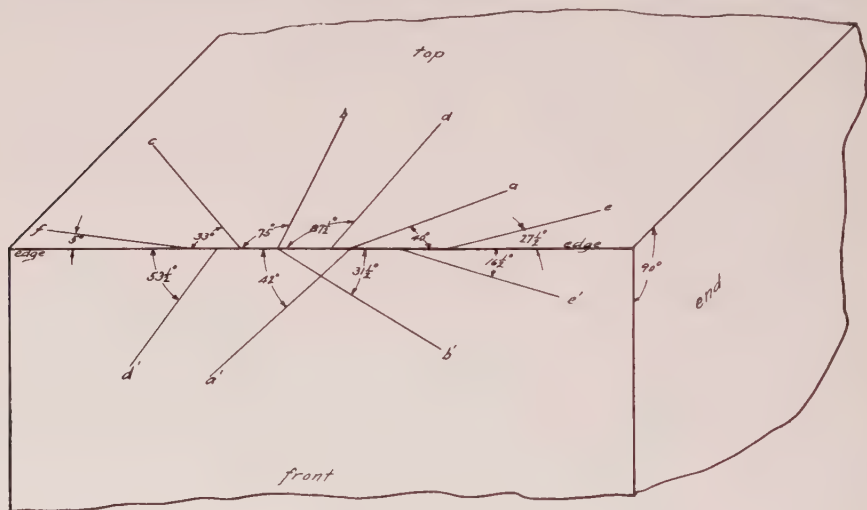
³ *Ibid.*, 187.

⁴ P. Groth: *Chem. Kristallographie* (1906, Pt. 1) 8, 10.

MEASUREMENTS ON BERYLLIUM CRYSTALS

A sketch showing the 10 angles measured on one of our beryllium crystals is given in Fig. 2. It will be observed that only two pairs of lines, representing twin bands, $a-a'$ and $b-b'$, are connected across the line marked "edge" in this figure. These were the only bands which could be matched by direct observation under the microscope. Similar relationships between the bands $d-d'$ on the one hand and $e-e'$ on the other were recognized during the subsequent analysis of the data.

In the stereographic projection, Fig. 3, the equatorial plane coincides with the horizontal plane (top) in Fig. 2 and the diameter marked "edge"



Beryllium 130A2.

FIG. 2.—ANGLES BETWEEN TWIN BANDS AND THE EDGE OF A BERYLLIUM CRYSTAL MEASURED IN TWO PLANES AT RIGHT ANGLES TO ONE ANOTHER.

represents the trace of the front vertical plane. The circles A , B , D , and E represent the poles of the planes aa' , bb' , dd' and ee' , respectively, of Fig. 2. The diameters F and C represent vertical great circles along which the poles of the planes f and c , which could only be measured on one surface, must be located. The following conclusions may be drawn from Fig. 3:

(1) The angles between any two poles A , B , D , and E correspond within a degree or two to the angles between planes of form $\{10\bar{1}2\}$ listed in column 3 of Table 2, indicating that the twin lamellae are parallel to these planes.

(2) The validity of the above conclusion may be proved beyond question by carrying out a further construction; viz., assume pole E to represent the exact location of one plane of form $\{10\bar{1}2\}$. Locate the best average position of the hexagonal axis at (0001) by estimating the true

point of intersection of four small circles constructed around the four poles A , B , D , and E at a radial distance of $42^\circ 22'$ (the angle between planes of form $\{0001\}$ and $\{10\bar{1}2\}$ as shown in column 3 of Table 2). On a small circle of this radius with pole at \odot and E as a starting point, the poles of successive planes of form $\{10\bar{1}2\}$ are encountered at intervals of $39^\circ 23'$ at the points marked X . The earlier conclusion is verified by the close correspondence between the theoretical locations and the four observed poles and further by the fact that the two additional poles

TABLE 2.—*Interplanar Angles in the Hexagonal Close-packed Lattice for Axial Ratios Corresponding to Be, Mg, Zn, and Cd*

From	To	Be $c/a=1.58$		Mg $c/a=1.624$		Zn $c/a=1.86$		Cd $c/a=1.89$	
		Angle	Supplement	Angle	Supplement	Angle	Supplement	Angle	Supplement
0001	$\{10\bar{1}2\}$	$42^\circ 22'$	$137^\circ 38'$	$43^\circ 9_2'$	$136^\circ 50_2'$	$47^\circ 2_2'$	$132^\circ 57_2'$	$47^\circ 30'$	$132^\circ 30'$
	$\{1\bar{1}24\}$	$38^\circ 18_2'$	$141^\circ 41_2'$	$39^\circ 5'$	$140^\circ 55'$	$42^\circ 55_2'$	$137^\circ 4_2'$	$43^\circ 23'$	$136^\circ 37'$
	$\{10\bar{1}\bar{1}\}$	$61^\circ 16_2'$	$118^\circ 43_2'$	$61^\circ 56'$	$118^\circ 4'$	$65^\circ 2'$	$114^\circ 58'$	$65^\circ 23'$	$114^\circ 37'$
	$\{1\bar{1}2\bar{2}\}$	$57^\circ 40'$	$122^\circ 20'$	$58^\circ 22_2'$	$121^\circ 37_2'$	$61^\circ 44'$	$118^\circ 16'$	$62^\circ 7'$	$117^\circ 53'$
10 $\bar{1}2$	$01\bar{1}2$	$39^\circ 23'$	$140^\circ 37'$	$40^\circ 0'$	$140^\circ 0'$	$42^\circ 56'$	$137^\circ 4'$	$43^\circ 16'$	$136^\circ 44'$
	$\bar{1}102$	$71^\circ 24'$	$108^\circ 36'$	$72^\circ 39'$	$107^\circ 21'$	$78^\circ 40'$	$101^\circ 20'$	$79^\circ 22'$	$100^\circ 38'$
	$0\bar{1}12$	$84^\circ 44'$	$95^\circ 16'$	$86^\circ 19'$	$93^\circ 41'$	$94^\circ 5'$	$85^\circ 55'$	$95^\circ 0'$	$85^\circ 0'$
	$\bar{1}012$	$36^\circ 6'$	$143^\circ 54'$	$36^\circ 45'$	$143^\circ 15'$	$39^\circ 49'$	$140^\circ 11'$	$40^\circ 10'$	$139^\circ 50'$
11 $\bar{2}4$	$\bar{2}114$	$64^\circ 56'$	$115^\circ 4'$	$66^\circ 11'$	$113^\circ 49'$	$72^\circ 17'$	$107^\circ 43'$	$73^\circ 0'$	$107^\circ 0'$
	$\bar{1}\bar{2}14$	$76^\circ 37'$	$103^\circ 23'$	$78^\circ 10'$	$101^\circ 50'$	$85^\circ 51'$	$94^\circ 9'$	$86^\circ 46'$	$93^\circ 14'$
	$\bar{1}\bar{1}24$	$52^\circ 0'$	$128^\circ 0'$	$52^\circ 22'$	$127^\circ 38'$	$53^\circ 54'$	$126^\circ 6'$	$54^\circ 4'$	$125^\circ 56'$
	$\bar{1}\bar{1}01$	$98^\circ 50'$	$81^\circ 10'$	$99^\circ 40'$	$80^\circ 20'$	$103^\circ 27'$	$76^\circ 33'$	$103^\circ 52'$	$76^\circ 8'$
10 $\bar{1}1$	$0\bar{1}11$	$122^\circ 33'$	$57^\circ 27'$	$123^\circ 52'$	$56^\circ 8'$	$130^\circ 4'$	$49^\circ 56'$	$130^\circ 46'$	$49^\circ 14'$
	$\bar{1}2\bar{1}2$	$49^\circ 59'$	$130^\circ 1'$	$50^\circ 24'$	$129^\circ 36'$	$52^\circ 16'$	$127^\circ 44'$	$52^\circ 28'$	$127^\circ 32'$
	$2\bar{1}\bar{1}2$	$94^\circ 4'$	$85^\circ 56'$	$95^\circ 0'$	$85^\circ 0'$	$99^\circ 24'$	$80^\circ 36'$	$99^\circ 54'$	$80^\circ 6'$
	$\bar{1}\bar{2}12$	$115^\circ 20'$	$64^\circ 40'$	$116^\circ 45'$	$63^\circ 15'$	$123^\circ 28'$	$56^\circ 32'$	$124^\circ 14'$	$55^\circ 46'$

occur on or very close to the diameters C and F , thus identifying the entire group of observed planes as the six possible twinning planes of form $\{10\bar{1}2\}$.

Observations made on two additional beryllium crystals gave similar results in somewhat less complete form owing to the smaller number of twin bands present in each case.

ANGLES MEASURED ON MAGNESIUM AND CADMIUM CRYSTALS

The angles measured on one of the magnesium crystals are shown in Fig. 4, and the corresponding projection in Fig. 5. As in the case of

beryllium, all of the possible twinning planes of form $\{10\bar{1}2\}$ are identified. Here, the pole of the plane, f' , whose only visible trace is normal to

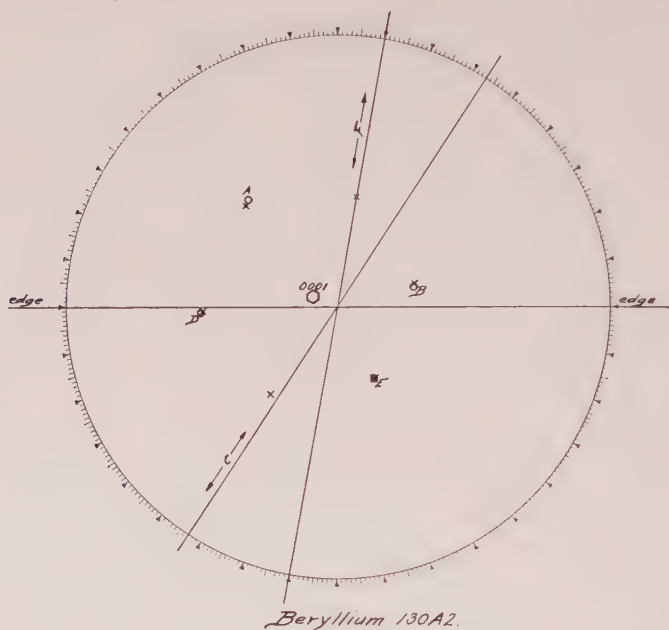


FIG. 3.—STEREOGRAPHIC PROJECTION OF THE DATA OBTAINED FROM FIG. 2.

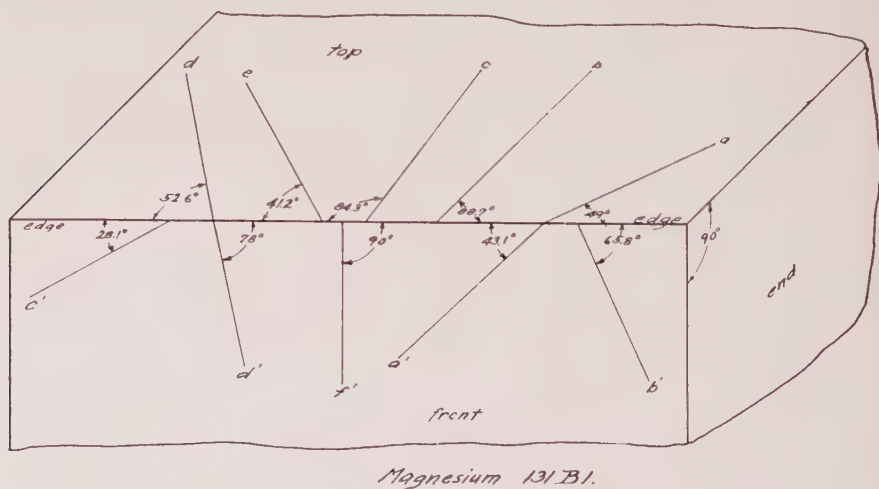
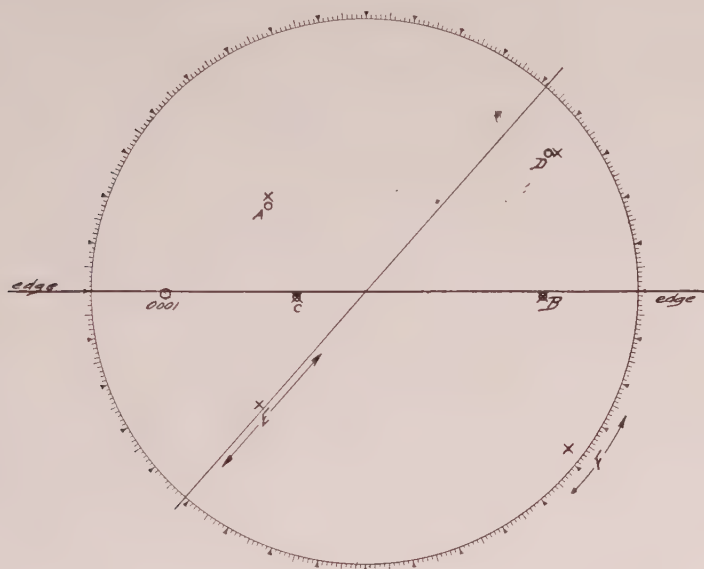


FIG. 4.—ANGLES BETWEEN TWIN BANDS AND THE EDGE OF A MAGNESIUM CRYSTAL MEASURED IN TWO PLANES AT RIGHT ANGLES TO ONE ANOTHER.

the horizontal(top) plane of Fig. 4, falls upon the divided circle (in Fig. 5). Assuming that the crosses at C and B in Fig. 5, which are separated by

one of the possible angles between planes of form $\{10\bar{1}2\}$, represent the true locations of two poles, the theoretical locations of the other four poles corresponding to planes of the same form are shown by crosses in the



Magnesium 131B1.

FIG. 5.—STEREOGRAPHIC PROJECTION OF THE DATA OBTAINED FROM FIG. 4.

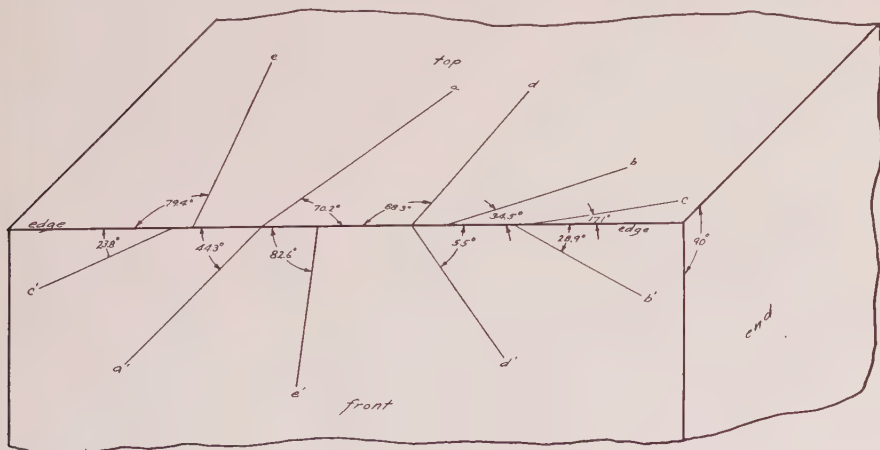


FIG. 6.—ANGLES BETWEEN TWIN BANDS AND THE EDGE OF A CADMIUM CRYSTAL MEASURED IN TWO PLANES AT RIGHT ANGLES TO ONE ANOTHER.

vicinity of *A*, *D*, *E*, and *F* in good agreement with the experimental data. The position of the corresponding hexagonal axis is also marked. Meas-

urements on two additional crystals of magnesium gave equally satisfactory results.

The experimental work with cadmium is illustrated in Figs. 6 and 7. Five of the poles representing planes of form $\{10\bar{1}2\}$ were definitely located in the projection. No trace of the sixth plane was seen in any surface under observation. The close agreement between theoretical and observed locations of these poles is evident on inspection of Fig. 7.

Twin lamellae in four additional cadmium crystals were also found to parallel planes of form $\{10\bar{1}2\}$.

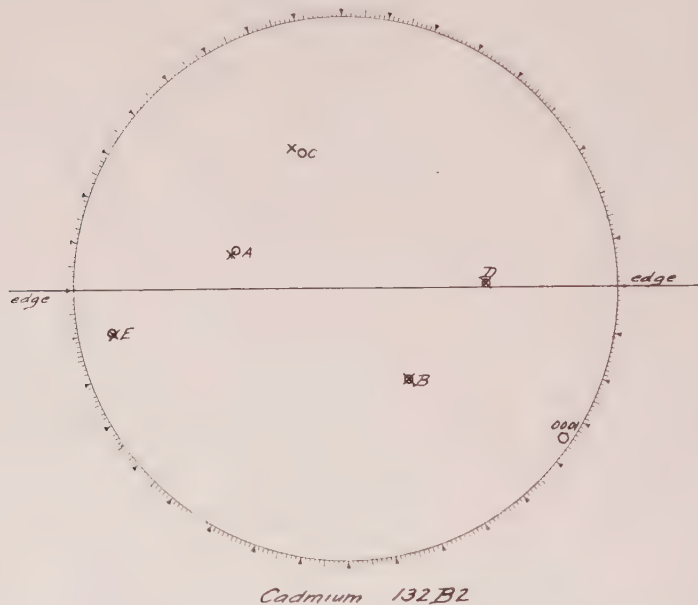


FIG. 7.—STEREOGRAPHIC PROJECTION OF THE DATA OBTAINED FROM FIG. 6.

CONCLUSION

It may be objected that the procedure adopted in all of these experiments identifies only the plane of composition between a twin lamella and the parent crystal without regard to the location of an axis of twinning. We can only urge that the twinning law, which has been precisely determined in the case of zinc, in all probability holds for the remaining metals of the group, since they exhibit a marked analogy of crystal structure and develop twin lamellae of similar appearance⁵ along composition planes of the same form.

⁵ We have not included photomicrographs of these structures, since they all correspond to the type abundantly illustrated in the papers referred to on the first page.

Twinning in Ferrite

BY L. W. MCKEEHAN,* NEW YORK, N. Y.

(Detroit Meeting, September, 1927)

THE occurrence of twins in large ferrite crystals, made by a new process, was reported in a recent note.¹ This paper describes a typical case of such twinning and suggests, on the basis of the observed facts, why smooth slip-planes are rarely observed in this metal.

METHOD OF PREPARATION

The material in which the crystals here dealt with were grown was made from $\frac{1}{8}$ -in. Armco iron welding rod containing C, 0.04; S, 0.037; P, 0.003; Si, 0.008, and Mn, 0.02 per cent. This rod was cold drawn into wire about 1 mm. dia. A piece of this wire was supported vertically and was locally heated in hydrogen at atmospheric pressure to about 1400° C. by an alternating current (60 cycles per sec.) of about 35 amp., passed through it between a pair of traveling contacts about 8 cm. apart. The rate of travel for the case in hand was 12 cm. per hr. After some 30 cm. of the length of the wire had been heated and cooled in this manner the whole wire was immersed for a few seconds in dilute nitric acid, not restrained by alcohol. Etching was continued until, as nearly as could be judged by eye, the original smooth cylindrical surface of the wire was no longer capable of specular reflection.

MEASUREMENTS

The wire in the etched state was next mounted in a goniometer of special form which allowed the measurement of the spherical coordinates of the normals to any plane surfaces left by the etching. These coordinates were most conveniently a polar distance, θ , from one direction of the wire axis, and an azimuth or longitude, ϕ , from an arbitrary prime meridian. The region to be described more particularly is shown at a low magnification in Fig. 1, which gives two different views, differently illuminated to show the spatial relationship of a crystal occupying most of the part shown and of an inclusion, or rather a series of three inclusions suspected of being twins based on the principal crystal.

* Bell Telephone Laboratories, Inc.

¹ L. W. McKeehan: Iron Crystals. *Nature* (1927) **119**, 705.

As has previously been noted,² the brightest reflecting surfaces left by this process of etching ferrite are planes of the form $\{100\}$. From a point of view through which a plane of this form can reflect light into the eye will then be seen a nearly uniform bright surface, sensibly flat although in fact it consists of parallel facets at different distances from the eye and inclined at different angles to the original cylindrical surface. The individual facets are not resolved by the naked eye, and this is a real advantage in making the settings for θ and ϕ .

Table 1 contains the goniometric data for the principal reflections from the major crystal (C) and from the inclusions (C') which show by

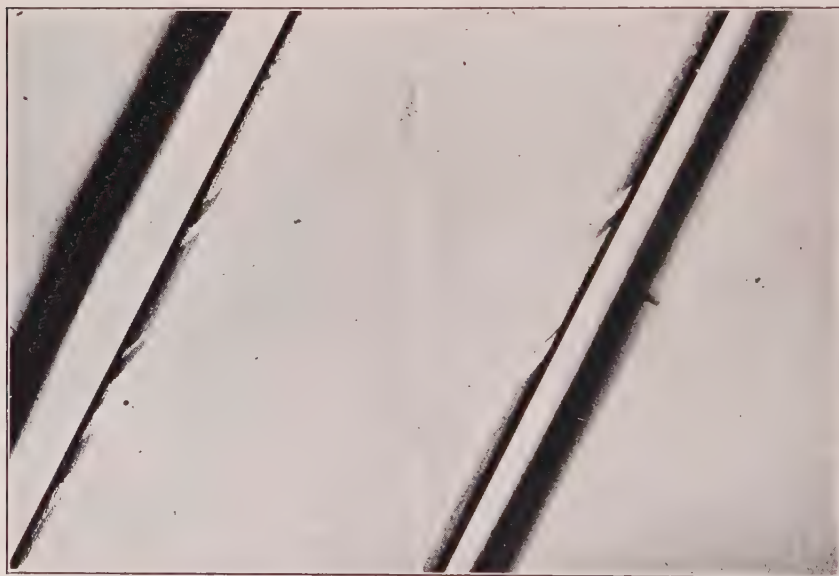


FIG. 1.—TWO VIEWS OF ETCHED WIRE. AT LEFT THE PRINCIPAL CRYSTAL IS BRIGHTER; AT RIGHT, THE TWINS ARE BRIGHTER. A SECOND SET OF TWINS APPEARS NEAR THE BOTTOM.

their simultaneous signals that they all have the same crystal axes. These data are plotted at the points of corresponding designation on the stereographic diagram, Fig. 2. The diagram is drawn on the equatorial plane $\theta = 90^\circ$, and the prime meridian, $\phi = 0^\circ$, is the half great circle WO . Great circles centered at X , Y and Z (full lines), and at X' , Y' , Z' (long dashes), show how nearly the observed reflections for each crystal lie at the theoretical angle (90°) from each other. There is a tendency for etched surfaces to lie more nearly parallel to the wire axis than they should. This is believed to be due to retarded attack in the deeper parts of etching pits. X-ray data show that no comparable lattice distortion really exists.

² L. W. McKeehan: *Op. cit.*

TABLE 1.—*Goniometer Data for Fig. 2*

Each Entry is the Average of Three Settings

	As Read		As Plotted		Designation
	θ	ϕ	θ	ϕ	
Principal crystal, <i>C</i>	137.2	223.1	42.0	46.5	<i>X</i>
	41.3	49.9			
	105.6	341.1	73.7	162.4	<i>Y</i>
	73.0	163.7			
	121.7	82.7	57.3	265.5	<i>Z</i>
	56.3	268.8			
Twins, <i>C'</i>	118.7	289.7	59.8	113.1	<i>X'</i>
	58.3	116.5			
	71.5	212.9	71.5	212.9	<i>Y'</i>
	138.7	153.5			<i>Z'</i>
	40.4	327.4	40.8	330.4	

Except for one set of planes reflections were obtained from both sides of the wire.
Plane of section, *P*, $\phi = 262.1^\circ$.

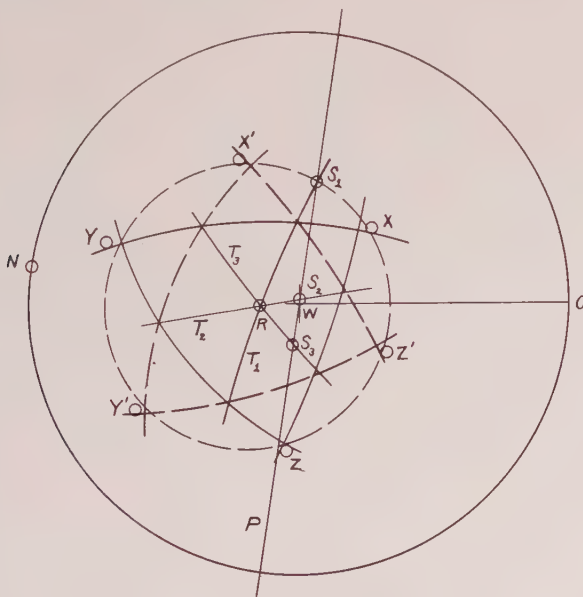


FIG. 2.—STEREOGRAPHIC DIAGRAM.

PROOF OF TWINNING

If the two crystals *C* and *C'* are twins related in the only way possible³ to the body-centered cubic structure of ferrite, the axes *X'*, *Y'*, *Z'* should

³ O. Mügge: Struktur und einfache Schiebungen des Eisens. *Zeitschr. f. anorg. Chem.* (1922) **121**, 68.

G. D. Preston: The Formation of Twin Metallic Crystals. *Nature*. (1927) **119**, 600.

be derivable from the axes X, Y, Z either by rotation through 60° about the center of the triangle XYZ , which is a line of closest atoms and has the form $[111]$, or by reflection in any one of the three planes of the form $\{211\}$ which intersect in this line. The point R of Fig. 2 is a point so



FIG. 3.—SECTION OF WIRE PARALLEL TO AXIS; POLISHED AND ETCHED. $\times 24$. SMALL CIRCLE INDICATES PART OF WIRE SHOWN IN FIG. 4.

chosen that it is the best rotation-axis for the first twinning operation just described. The three great circles T_1, T_2, T_3 are selected at 120° to each other as the best planes of form $\{211\}$ in both crystals which intersect in R . The complete circle of dashes is drawn with pole at R and radius

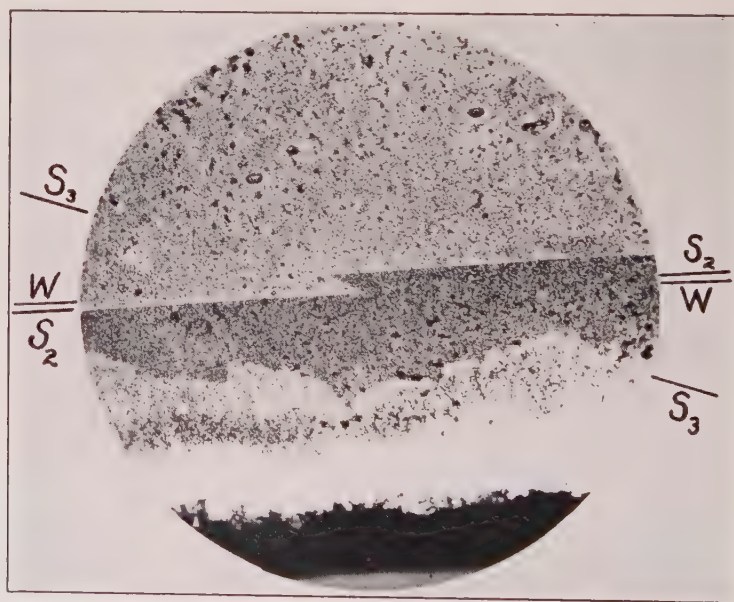


FIG. 4.—SECTION OF WIRE; POLISHED AND ETCHED. $\times 100$.

$54^\circ.7$; it is the circle which would, in case the data were exact, pass through all six of the cubic axes, three in each of the twins. How well the data agree with the theoretical relations between twins may be judged by inspection.

The boundaries between the twins should, of course, be planes of the form $\{211\}$. The positions of these planes are not easy to determine in the case of a cylindrical specimen so to make measurement easier the wire was sectioned parallel to its axis, W , polished, etched and rephotographed both at a low power, as in Fig. 1, and at a higher power. These photographs are shown in Figs. 3 and 4, the part shown in Fig. 4 being shown on

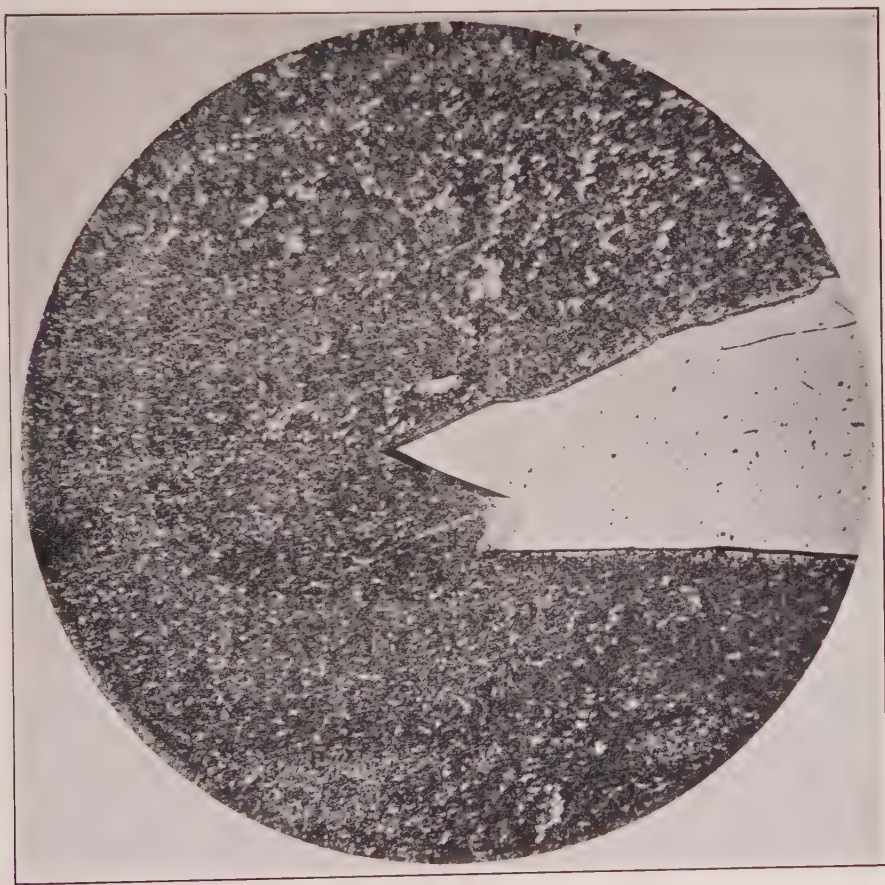


FIG. 5.—TWIN BOUNDARY IN FERRITE. $\times 100$.

Fig. 3 by a small circle. The penetration of the presumably twinned portion into the body of the wire is clearly evident, and Fig. 4 especially shows that some at least of the twin boundaries are planes, or rather that they have straight-line traces on the (arbitrary) plane of section.

The plane of section was fixed by further measurements in the goniometer and is shown in Fig. 2 by the line P , the normal being at the point N . The three possible twinning planes cut the plane P at the points S_1 , S_2 , S_3

which lie at 48.5° , 1.6° and 17.8° , respectively from W . This means that twin boundaries in the plane of section can only lie at these angles to the wire axis. Fig. 4 shows how nearly some of the observed boundaries fit this condition. The lines $W-W$, S_2-S_2 and S_3-S_3 have the orientations obtained from Fig. 2. It should be observed that the angles WS_1 and WS_3 are particularly sensitive to errors in the fixation of N . Other observed angles in the plane of section agree better with those predicted than does the angle shown in Fig. 4. It is to be concluded that the crystals here measured are twins in the crystallographic sense.

There are four different ways of twinning on a given body-centered cubic crystal, one associated with each threefold axis (of the form $[111]$). In the cases which have been analyzed the threefold axis on which twinning actually takes place is that one which permits twinning on the $\{211\}$ plane most nearly containing the wire axis. So few pairs have been tested, however, that this coincidence may be fortuitous.⁴

COMPARISON WITH PREVIOUS WORK

The conditions at temperatures in the neighborhood of the Ar_3 point (say 900° C.) where these twins originated are apparently much more favorable to the formation of large twins than are conditions at room temperature where even large crystals do not frequently suffer deformation twinning, though signs of such behavior have been noted.⁵ The peculiar relation of twins in a body-centered cubic structure may afford an explanation for the apparent absence of twinning under continued stresses. As we have seen it is possible in ferrite (as it is not in face-centered cubic metals) to have zigzag twin boundaries. Such zigzag boundaries on a fine enough scale would not be recognizable as twin boundaries and might easily suggest columnar slipping⁶ as opposed to plane slipping. The coherent columns, if the behavior at room temperature is interpreted as due to repeated twinning, would be prisms whose parallel elements are $[111]$ lines and whose narrow plane faces are $\{211\}$

⁴ Fig. 5 ($\times 100$) shows another case in which the principal crystal, dark in this view, had the wire axis nearly in a $[100]$ direction. A twin, bright in this view, is seen in which the two boundaries at the apex are of the form $\{211\}$, these being the planes of this form passing closest to the wire axis. The horizontal line below the apex appears to be the trace of a plane of form $\{110\}$ in each of the crystals. This cannot be a twinning plane in the ordinary sense, however, since the arrangement of atoms on one side is not simply related to that on the other. It is perhaps made up of short steps of the two twinning planes equally inclined to the $\{110\}$ plane. If these steps exist they are not optically resolved.

⁵ H. O'Neill: Deformation Lines in Large and Small Crystals of Ferrite. *Jnl. Iron Steel Inst.* (1926) **113**, 417.

⁶ G. I. Taylor and C. F. Elam: The Distortion of Iron Crystals. *Proc. Roy. Soc.* (1926) **112A**, 337.

planes, three different planes of this type being available—each as often as necessary—to bound any given column.

STABILITY OF TWIN BOUNDARIES

It has been pointed out by Preston⁷ that a twin boundary in ferrite must be the locus of some distortion, since the atom centers cannot maintain unaltered intervals right up to the common plane. It was therefore suspected that on reheating a pair of twins to temperatures above the recrystallization temperature but below the A_3 point new crystals might appear at the twin boundary or that one of the twins might grow at the expense of the other. The piece of wire described above was therefore heated in vacuum at 700° C. for 3 hr. after the first set of goniometer measurements, and was then reexamined under the microscope. No change in the appearance of the boundary was detected. The photograph of the section, Fig. 4, at higher magnification, which was taken after this heat-treatment, shows even more clearly that the twin boundary remains plane under these conditions known to be favorable to crystal growth in strained ferrite. It is concluded that the degree of distortion at the twin boundary is insufficient to provide nuclei for crystal growth or that the adjacent crystals are too perfectly free from strain to be absorbed to any appreciable depth by such nuclei in the time available. In either case twin boundaries in ferrite are decidedly more stable than those in zinc where it is known that comparable treatment causes their effacement.⁸

DISCUSSION

Z. JEFFRIES, Cleveland, O.—It is indeed very interesting to find that a body-centered cubic metal can twin, under certain conditions at any rate, although the production of what has been called Neumann bands in alpha iron has been known for many years and the explanation of that seems to be tied up with some sort of twinning arrangement, as has been worked out pretty thoroughly in England in the last few years.

A. ST. JOHN, Long Island City, N. Y.—It seems to me that passing from the ordinary method of representing the face-centered cube to this method is exceedingly valuable. It brings out clearly that in the face-centered cube each atom is surrounded by 12 others just as near to it and to each other as they can possibly get. Hence there are difficulties in reducing the dimensions of a face-centered lattice by the occasional substitution of smaller atoms unless a compression or distortion of the atoms themselves takes place. In view of the present belief that an atom is like a miniature solar system, this is reasonable, and it is convenient to think of the atoms as behaving like little balloons, normally spherical but assuming other shapes when persuasive forces are applied.

⁷ G. D. Preston: *Op. cit.*

⁸ C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 143.

C. F. ELAM, London, Eng.—I have been working out some twin structures in copper and aluminum. I find in the case of aluminum, that the two parts of the twin, on the two samples I have examined, have the same relationship to each other, but are not twins in the crystallographic sense of the word. The two parts appear to be reversed and rotated 60° on a dodecahedral plane, but in ordinary cubic crystals that is not a possible form of twinning. I have come to the conclusion that these crystals have all the appearance of twins, but are not twins at all.

I have only examined one "twin" in copper, up to the present, but I find the two parts have no direct relationship. In both metals the twin boundary is not a crystal plane, nor has it any crystallographic relation to either crystal.

I was very interested to find that Dr. McKeehan had very good evidence in the case of iron, that these were genuine twins. I think the only way to settle the question in other metals is to get specimens that show banding sufficiently large for both X-ray and external measurements.

O. E. HARDER, Minneapolis, Minn.—In the paper on twinning in ferrite, in both the face-centered and body-centered lattices, the author mentioned that the plane of slippage was the plane of highest atomic population. I would like some opinion with reference to whether the slippage in the plane is due to high atomic population or whether it is more influenced by a large interplanar distance between the planes of highest atomic population.

L. W. MCKEEHAN.—I wish first to agree with Miss Elam's statement that in proving twinning X-ray analysis is sufficient but not necessary. If the parts of the supposedly twinned structure are so large that crystallographic methods can be applied to both parts, one can establish the twinning without X-rays. Facets, recognizable by their number and position on the sphere of reference as belonging to a certain family of planes, can be recognized in both the base structure and the "twin," and one can then be fairly sure whether or not one part is twinned with respect to the other. I have, however, tried both methods and have no objection to the X-ray method. It is the only one possible where the crystals are so small or so placed that one cannot see them well.

In regard to the last question, I cannot distinguish between high atomic population in each of a set of planes and great interplanar distance, because these two things are mathematically related, their product giving the number of atoms per unit volume. Whether the plane of easy slip in the case of iron is the twinning plane here found I am not so sure either, because the plane of easy slip is very hard to agree upon. Some people think that the $\{211\}$ plane is the one in which slipping occurs, and others have a different view.

In the case of face-centered cubic metals I am interested to hear from Miss Elam that what appear to be twins are not always so in reality. I have no evidence of my own on that point.

Magnesium—Its Etching and Structure

By H. B. PULSIFER,* CLEVELAND, OHIO

(New York Meeting, February, 1928)

ABOUT 15 varieties, or modifications, of the best magnesium available were prepared and subjected to etching tests, then examined for microstructure. Of the 30-odd etching reagents that were tried, nearly half, mostly ammonium salts, etched the metal satisfactorily. The surfacing and etching of magnesium is shown to be a very simple and quick operation.

The density and hardness of magnesium were determined. The most interesting new observations relate to the finding of the hexagonal etch figures, the crystal laminations, and the fact that the metal is plastic, cold, when restrained or quickly deformed. Under slowly applied pressure cold metal deforms slightly, then shears to fracture without plastic flow.

The chief structural features of magnesium are presented in two reduced photographs and 30 photomicrographs.

MATERIALS TESTED

There are only two sources in the United States from which new metal can be procured: the American Magnesium Corpn. and the Dow Chemical Co. No pronounced structural or property differences in the metals from these two companies were disclosed by the work of this investigation. The following materials were obtained from the manufacturers:

1. Massive crystals of distilled metal (American Magnesium Corpn.).
2. Rods of hot-extruded metal, $\frac{1}{2}$ -in. squares and $\frac{5}{8}$ -in. rounds (American Magnesium Corpn.).
3. Sheet magnesium, 0.005-in. thick (American Magnesium Corpn.).
4. Cast stick metal, $1\frac{3}{8}$ -in. dia. (Dow Chemical Co.).
5. Magnesium-aluminum alloy, hot-rolled plate, $\frac{1}{2}$ -in. thick (American Magnesium Corpn.).

From these materials, were prepared:

6. Sections from a furnace-cooled ingot made from distilled crystal.
7. Cold-strained pieces from (6), (4) and (2).
8. Pieces cold-squeezed to fracture from (6), (4) and (2).
9. Hammer-struck pieces from (6), (4) and (2).
10. Steam-hammer struck pieces from (6), (4) and (2).
11. Sections from furnace-cooled ingot of the magnesium-aluminum alloy.

* Metallurgist, Ferry Cap & Set Screw Co.

COMPOSITION OF THE MATERIALS

No analyses were made for this work. The distilled crystals were very bright and lustrous. Since they are produced by the condensation of vapor rising from metal heated to less than its normal boiling point (1120° C.) and *in vacuo*, there are practically no impurities present. The metal is diamagnetic and of excellent appearance under the microscope. The manufacturers claim a purity of 99.99 per cent. for this material.

The Dow stick metal is represented as 99.95 per cent. pure.

The particular magnesium-aluminum alloy used was represented as containing: magnesium, 95.45 per cent.; aluminum, 4.0 per cent.; manganese, 0.4 per cent.

In its handbook entitled "Magnesium," the American Magnesium Corpn. (1923) states that the tensile strength of pure cast magnesium is 13,000 lb. per sq. in.; its proportional limit is 500 lb. per sq. in.; and that elongation and reduction of area are both 6 per cent. Extruded and rolled pure metal may have a tensile strength as high as 28,000 lb. per sq. in.; the proportional limit may be as high as 2500 lb. per sq. in., and elongation and reduction of area up to 8 per cent.

The 4 per cent. aluminum alloy has a maximum tensile strength of about 40,000 lb. per sq. in., proportional limit a maximum of 7500 lb. per sq. in. and elongation 20 per cent. with 33 per cent. maximum reduction in area.

ETCHING MAGNESIUM

Magnesium responds to chemical attack in a variety of ways. The metal is temporarily inert in solutions of hydrofluoric acid, sodium acid fluoride, sodium acetate, chromic anhydride and some potassium salts.

Magnesium dissolves violently in all concentrations of aqueous hydrochloric acid, in many concentrations of nitric acid, and less violently in sulfuric acid, either dilute or concentrated. A passive resistance to nitric acid may be followed by violent solution. A brown stain that is sometimes left is one objection to nitric acid.

The best etching seems to be produced when solution is slow and the evolution of gas bubbles is active but not too vigorous. This obviously means a general surface attack. Whenever the gas evolution is slowed down to a few bubbles now and then it probably means pitting and local corrosion. The best type of etching occurs in solutions of sodium carbonate and bicarbonate, dilute acetic acid, tartaric acid, concentrated acids dissolved in alcohol or acetone, and solutions of ammonium salts. The permissible ranges in concentration are evidently very wide. They were not accurately controlled in this work since it was neither convenient nor necessary.

To the naked eye, or microscopically, there are two widely different effects produced by the reagents that give acceptable results. There is the brilliant, glossy finish typified by the attack of concentrated nitric acid or hydrochloric acid in acetone and there is the dull, frosted finish made by dilute acetic acid and many ammonium salts.

TABLE 1.—*Effect of Etching Reagents on Magnesium*

Reagent	Action	Selec- tivity	Grain Bounds	Pits	Recom- mended
HNO ₃ , concentrated	yes	yes	finely	some	no
dilute,	yes	yes	finely	yes	no
conc., in alcohol,	yes	good	finely	no	yes
conc., in acetone,	yes	good	finely	no	yes
HCl, any concentration,	yes	no	some	yes	no
conc., in alcohol,	yes	yes	finely	no	yes
conc., in acetone,	yes	yes	finely	no	yes
HF, dilute,	no	no	no		no
H ₂ SO ₄ , dilute,	yes	yes	fair	some	no
conc., in alcohol,	yes	fair	fair	no	no
conc., in acetone,	yes	fair	good	some	no
Acetic acid, glacial,	yes	yes	irreg.	yes	no
dilute,	yes	yes	broad	some	yes
with nitric in acetone,	yes	yes	finely	no	yes
with chromic,	yes	no	poor	yes	no
Oxalic acid, dilute,	yes	poor	finely	yes	no
Tartaric acid, dilute,	yes	good	good	no	yes
Chromic acid, dilute,	no	no	no		no
with nitric, dilute,	yes	no	poor	yes	no
with hydrochloric, dilute,	yes	no	poor	yes	no
Ferric chloride, acid,	yes	no	no	badly	no
Ammonium chromate, dilute,	no	no	no		no
KCl, dilute,	no	no	no		no
KBr, dilute,	no	no	no		no
KNO ₃ , dilute,	no	no	no		no
K ₂ SO ₄ , dilute,	some	no	no	yes	no
K ₂ CO ₃ , dilute,	some	no	no	yes	no
NaCl, dilute,	yes	no	no	yes	no
Na ₂ SO ₄ , dilute,	some	no	no	yes	no
NaNO ₃ , dilute,	some	no	no	yes	no
Na ₂ CO ₃ , any concentration,	yes	yes	good	no	yes
NaHCO ₃ , any concentration,	yes	yes	good	no	yes
Sodium acetate, dilute,	no	no	no		no
NaOH, dilute,	no	no	no		no
NH ₄ HF ₂ , dilute,	no	no	no		no
NH ₄ Cl, dilute,	yes	yes	good	no	yes
NH ₄ NO ₃ , dilute,	yes	yes	good	no	yes
Ammonium sulfate,	yes	yes	good	no	yes
Ammonium carbonate, dilute,	yes	yes	good	no	yes
Ammonium acetate, dilute,	yes	yes	good	no	yes
Ammonium oxalate, dilute,	yes	yes	good	no	yes

The glossy, burnished surface is smooth and broken by major features only. The grain boundaries are hair-fine and Neumann lines appear as phantom markings. The frosted surface is due to a detailed and more minute attack that discloses the laminations and etch figures in each crystal unit. Grossly, the surface appears striated. The striations may interlace and occur in three directions. Neumann lines appear boldly.

Intermediate stages between the glossy and frosted finishes are present in all degrees, depending on the reagent, its concentration, and the time of immersion. One crystal plane etches smoothly when all others are rough; this is believed to be the basal plane of the hexagonal prism and it must, of course, occur parallel or nearly parallel to the surface of the specimen.

A peculiar and useless type of attack results from the immersion of a specimen in a solution of chromic anhydride and one other acid. In this instance the attack localizes, presumably at inclusions or defects, and deep cavities are dissolved out of the metal. The gas evolution may be of about the right intensity. The surface of the metal about the holes will be entirely passive and unaffected but inside the cavities the attack is selective so that when the specimen has been dried the lining of the holes reflects light from innumerable and brilliant crystal facets.

Table 1 gives a summary of the etching tests. The columns indicate whether or not there is chemical attack, if the attack is selective as to structural features, how grain boundaries are delineated, if pitting occurs, and whether the reagent is recommended.

In general, dilute acetic acid, ammonium salts, sodium carbonate and sodium bicarbonate give high relief and minute details. Tartaric acid in water and hydrochloric and nitric acids in alcohol or acetone give low relief, flat surfaces, hair-fine grain borders, little pitting and no staining or deep corrosion in the case of the alloy. The hexagonal fine structure has been seen best on specimens immersed in acetone to which enough concentrated sulfuric acid was added to give a normal gas evolution.

THE STRUCTURES

No entirely new appearances were found in magnesium. The dendrites, equiaxed grains, Neumann markings, slip zones and etch figures are similar to those found in other metals, especially zinc, cadmium and beryllium. The heavily cold-flowed zones were not studied in enough detail to establish the minute character of the metal. The laminations in the dendrites and equiaxed units are easily established but no tests were made to confirm whether a lamination sheet or the whole bundle of sheets should be considered the crystal unit.

A piece of the crystalline mass as loosened from the distillation retort is shown in Fig. 1 at one-half natural size. At the base the crystals are small and short. About $\frac{1}{8}$ in. out the crystals begin to be columnar,

feathery, and loosely adherent. Voids, blunt-ended suture lines and Neumann markings are common details. The single units are not as large as might appear at first glance; many interwoven and twisted crystal fibers make up what is a crystal strand.

A section through the ingot that was made from the distilled crystals, etched with dilute acetic acid and reduced to half size, is shown in Fig. 2. The author had previously noted the distinctly laminated structure of cast pure beryllium as shown in Fig. 3 at 500 dia. magnification. The piece of cast beryllium was etched with dilute hydrofluoric acid and showed the laminations and hexagonal etch-figures well because the basal plane of one crystal unit occurred parallel with the surface of the specimen. It is seen that hexagons are pyramided, one above another.

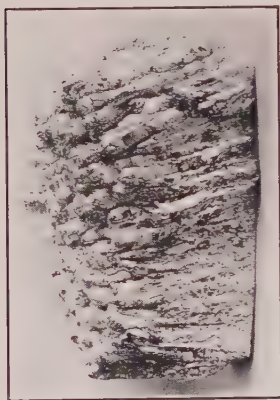


FIG. 1.—CRYSTALS OF DISTILLED MAGNESIUM AS TAKEN FROM RETORT. REDUCED ONE-HALF.

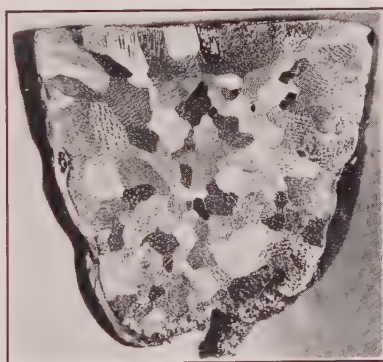
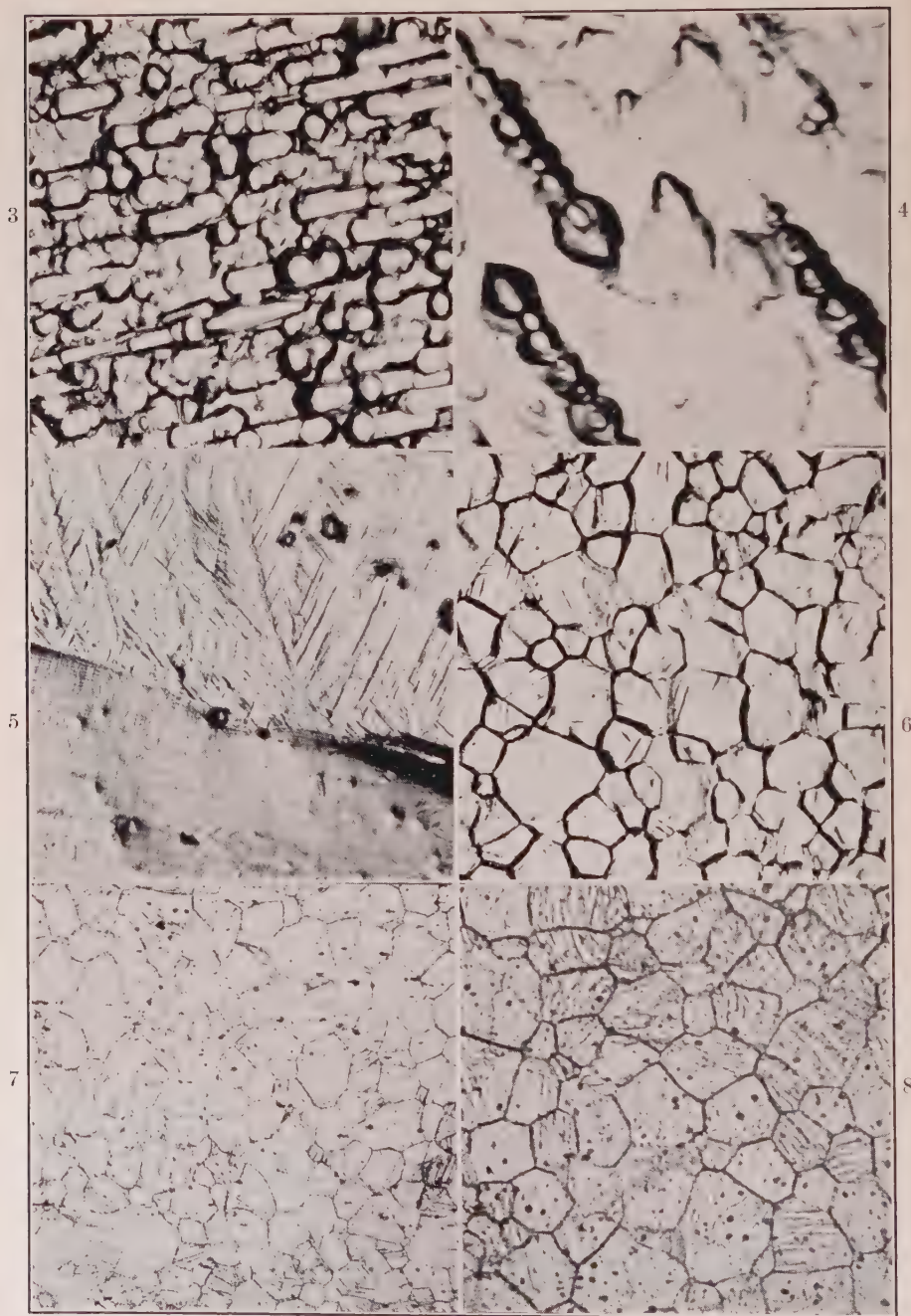


FIG. 2.—VERTICAL SECTION THROUGH FURNACE-COOLED INGOT MADE FROM DISTILLED CRYSTALS. ETCHED WITH DILUTE ACETIC ACID AND REDUCED ONE-HALF.

A similar, although not as crowded condition, is seen in the case of magnesium in Fig. 4. This is a detail at 1000 dia. magnification from one of the center units of Fig. 2. Rows of pyramids of hexagons appeared everywhere on this crystal face.

A boundary between two of the fibers of the distilled crystals is shown in Fig. 5 at 100 dia. Neumann markings are well developed on one of the crystals; somewhat more than the usual number of inclusions appear in both units.

The usual grain size and shape in the hot-extruded metal is shown in Figs. 6, 7 and 8. All are at 100 dia. magnification. Fig. 6 is a very good example of the results obtainable by etching with sodium bicarbonate solution. The print given in Fig. 7 typifies the fine lines and low relief obtainable with concentrated nitric and acetic acids in acetone. The somewhat greater delineation of Neumanns and the increased



FIGS. 3 TO 8.

amount of pitting shown in Fig. 8 is characteristic of etching with glacial acetic acid.

The differential etching of grain borders that sometimes gives partly broad and partly fine lines is indicated in detail in Fig. 9, which is from the same surface as Fig. 8, but at 1500 dia. magnification. The slope of the laminations determines the exposure to solution and so accounts for the differences in boundary width.

The usual size and contour of the grains in hot-extruded metal as etched with dilute acetic acid is portrayed in Fig. 10 at 250 dia. The surface of the grains does not show more than a rounded over fine structure, although some markings are present. All of the metal that was sectioned and examined showed abundant longitudinal streaks. Sometimes the streaks appear to be due to small grains of which the growth has been inhibited by the presence of many fine inclusions. At times the inclusions themselves appear to constitute the streak and interrupt normal grain size; at times gross imperfections interrupt the physical continuity of the rod. Fig. 11 shows a very common condition in this stock.

The Dow ingot had a finer dendritic structure than the furnace-cooled ingot from sublimed crystals. The dendrites were elongated and in radial position about the central axis. A section through some of the smaller units, cut parallel to the surface and near the outside, is shown in Fig. 12. The specimen was etched with sodium bicarbonate solution and the magnification is 100 diameters.

The Neumann markings occur frequently in all the specimens examined. There was no hint that resurfacing caused more markings to develop or that the surfacing operations caused those that were found. In the sublimed, cast, annealed, and slightly strained stock the Neumanns are clean cut and straight (Fig. 13). In heavily cold-flowed stock they are more thickly packed and curved (Fig. 14), sometimes short and blocky (Fig. 15).

The hot-deformed pieces of ingot did not recrystallize uniformly. New small crystals appeared in zones, probably the zones of maximum movement during the deformation. Fig. 16 shows a zone of the small, new units between patches of unaltered stock in a dendrite of the Dow ingot. This surface was etched with nitric and acetic acids in acetone and

FIG. 3.—HEXAGONAL MOTIF OF ETCH-FIGURES IN PURE CAST BERYLLIUM. ETCHED WITH HYDROFLUORIC ACID. $\times 500$.

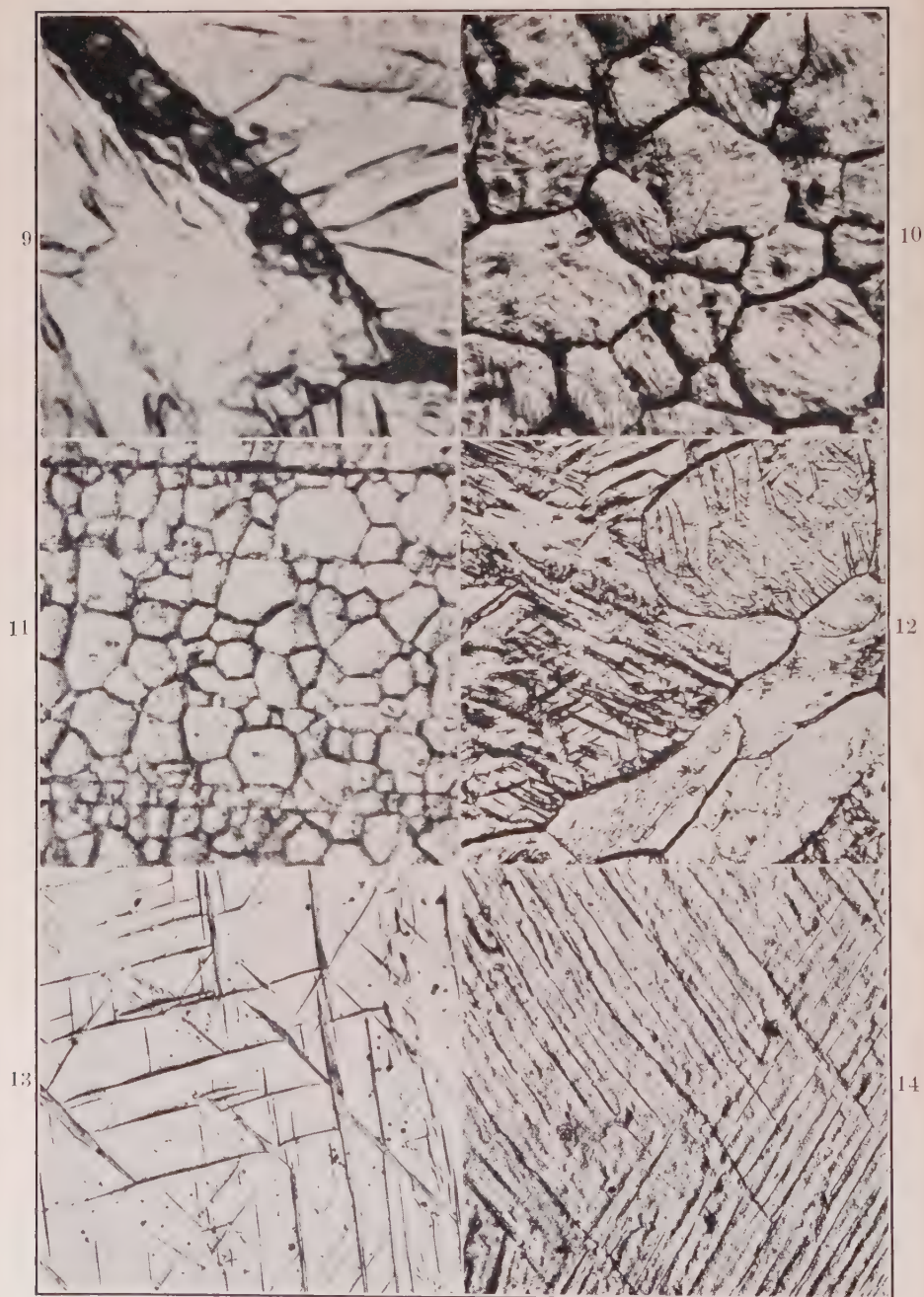
FIG. 4.—ROWS OF PYRAMIDS OF HEXAGONAL PLATES FROM ONE OF THE CENTRAL UNITS OF FIG. 2. $\times 1000$. B. & L., 1.9 MM. FLUORITE OBJ., 1.3 N. A., OIL IMM.

FIG. 5.—CRYSTAL BOUNDARY IN DISTILLED CRYSTALS (FIG. 1). ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 6.—HOT-EXTRUDED METAL, TRANSVERSE SECTION. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 7.—HOT-EXTRUDED METAL, LONGITUDINAL SECTION. ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. $\times 100$.

FIG. 8.—HOT-EXTRUDED METAL, TRANSVERSE SECTION. ETCHED WITH GLACIAL ACETIC ACID. $\times 100$.



FIGS. 9 TO 14.

magnified 250 dia. The appearance of these zones of recrystallized metal was one of the more difficult structures to record satisfactorily. The reagents that etch roughly, as acetic acid and ammonium salts, failed to show the units clearly; the low-relief reagents also failed to make the fine grain boundaries appear distinctly. The magnification of 250 dia. shows the units fairly well without excluding the zonal effect of their occurrence.

The cold-deformed and reheated stock underwent complete recrystallization. The results were all similar for the temperatures and times tried. Large and small grains appear in no apparent order. Fig. 17 shows the glossy surface produced by the concentrated nitric acid etching on a piece of the ingot from sublimed crystals. This piece was cold-squeezed, then heated to 380° C. for 3 hr. Fig. 18 is from a piece of the Dow ingot that was heated to 425° C. for 3 hr. after cold squeezing. Fig. 19 is from another piece of the Dow ingot that was squeezed and then heated to 500° C. for 30 min. The last two surfaces were etched with sodium bicarbonate solution. All three prints are at 100 dia. magnification.

The magnesium foil showed only a granular texture at low magnifications. At 1000 dia. the structure appears sharply. A fluorite objective, 1.9 mm., 1.3 N. A., and cedar-oil gap was used for this and higher magnifications. Fig. 20 shows large and small grains in the magnesium foil at 1000 dia. after etching with sodium bicarbonate. The very fine texture of the material might well account for its increased strength and hardness.

A limited amount of cold deformation does not appreciably alter the previous grain structure although a few sharp, new Neumanns may appear. Fig. 21 is a section normal to the compression in a piece of hot-extruded rod that was squeezed endwise. The specimen was etched with nitric and acetic acids in acetone and the magnification is 100 dia. A sledge-struck piece of the same rod, compressed laterally, gave the innumerable slip markings seen in Fig. 22. These markings are again in a plane normal to the compression; they are also at right angles to large shear fissures that opened in the metal.

One of the most interesting observations came on examination of a fracture zone in the same hammer-struck piece. The metal was not

FIG. 9.—DETAIL OF GRAIN BORDERS FROM SAME SURFACE AS FIG. 8. $\times 1500$. ETCHED WITH GLACIAL ACETIC ACID. B. & L. 1.9 MM. FLUORITE OBJ., 1.3 N. A., OIL IMM.

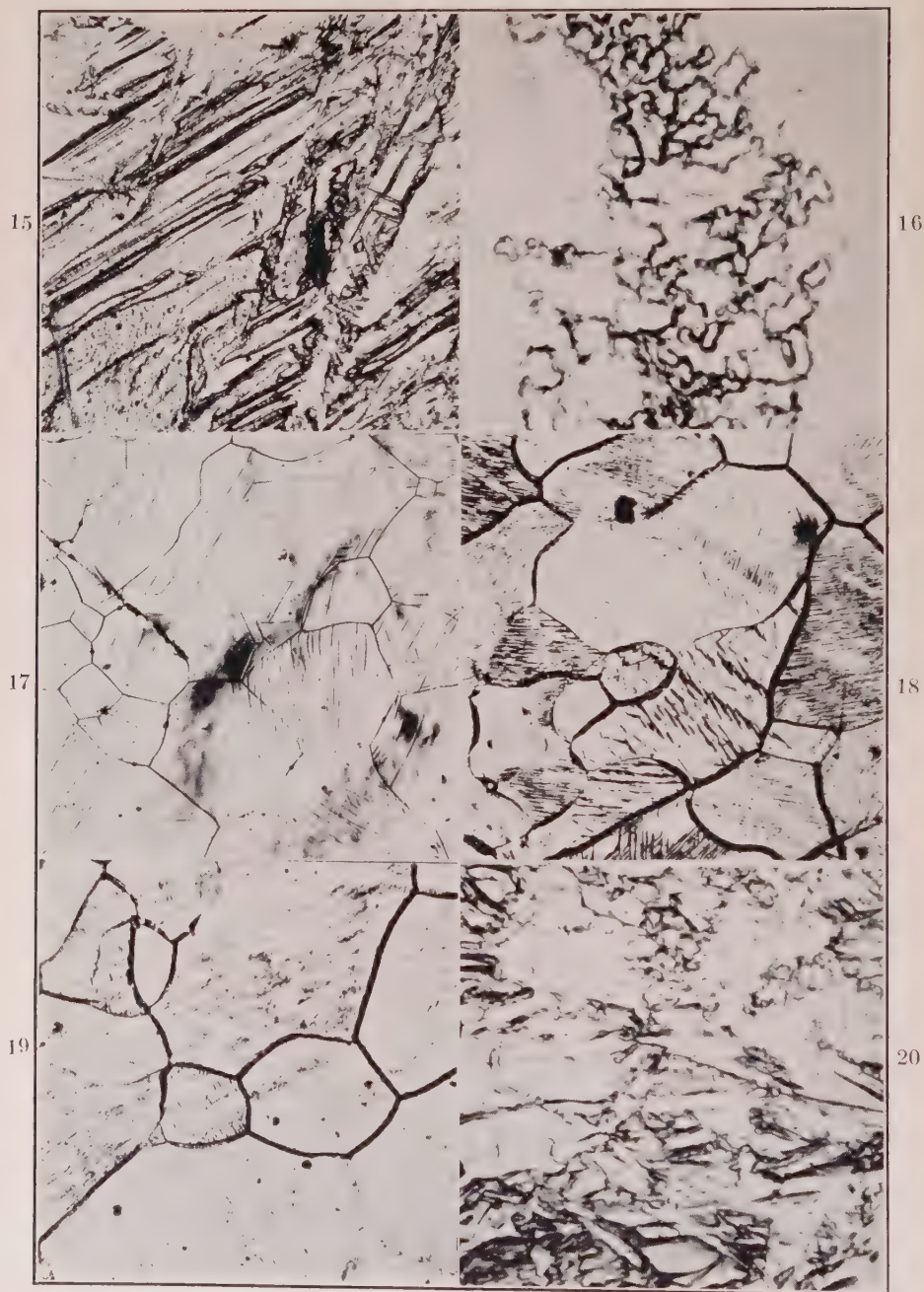
FIG. 10.—HOT-EXTRUDED MAGNESIUM ETCHED WITH DILUTE ACETIC ACID AND A FINAL DIP IN BICARBONATE SOLUTION. $\times 250$.

FIG. 11.—HOT-EXTRUDED MAGNESIUM, LONGITUDINAL SECTION. ETCHED WITH DILUTE ACETIC ACID. $\times 100$.

FIG. 12.—SECTION NEAR AND PARALLEL TO SURFACE OF DOW INGOT, ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 13.—NEUMANN MARKINGS ON CRYSTAL OF DOW STICK METAL AFTER SLIGHT COMPRESSION. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 14.—NEUMANNS IN CRYSTAL OF INGOT FROM SUBLIMED CRYSTALS AFTER COLD COMPRESSION. ETCHED WITH AMMONIUM ACETATE SOLUTION. $\times 100$.



FIGS. 15 TO 20.

entirely severed but hung together by a section in the center. At the original top and bottom surfaces the metal sheared apart with hardly any flowing of the metal bordering on the fissure. In the center of the piece the flowed metal layer increased to over 0.01 in. thick. Moreover, at the center, the metal had flowed enough to compensate for the movement and there was no fissure. Fig. 23 shows this zone of flowed and sheared metal at 100 dia. after etching with nitric and acetic acids in acetone. The print was taken at the end of the open fissure. The fine line continuing the fissure ended shortly beyond the field of the print and then a section of unbroken but heavily flowed stock extended to where the break commenced again on the other side. At the edges of the piece, where movement had been least restrained, the metal was sheared wide open; in the center, with restraining metal all about, the magnesium flowed instead of rupturing.

Following this discovery, other pieces of magnesium were deformed even more quickly with single blows of a large steam hammer. The pieces fractured much less than those struck with the sledge. They much resembled hot-deformed metal except that the free edges were serrated with sharp shear offsets.

The laminated structure of the ordinary equiaxed grains of hot-extruded metal is clearly shown in Figs. 24 and 25. In Fig. 24, taken at 1500 dia. with the fluorite, oil-immersion objective, the small etch figures are granular and irregular but the laminations appear sharply. The surface was etched with ammonium nitrate solution. Fig. 25 is at 2000 dia. and shows the laminations and granules less sharply; this surface was etched with dilute acetic acid.

SURFACING AND ETCHING

The three prints, Figs. 26, 27 and 28, are included to illustrate how quickly and easily magnesium is prepared for microscopic study. In general, the metal is prepared with comparatively little effort. High-speed wheels, mechanical elimination of scratches and prolonged buffing might be used but are hardly necessary. A surface that has been filed

FIG. 15.—HEAVY AND INTERLACING NEUMANN'S IN SECTION FROM DOW INGOT, MORE COMPRESSED THAN IN FIG. 13. ETCHED WITH AMMONIUM ACETATE SOLUTION. $\times 100$.

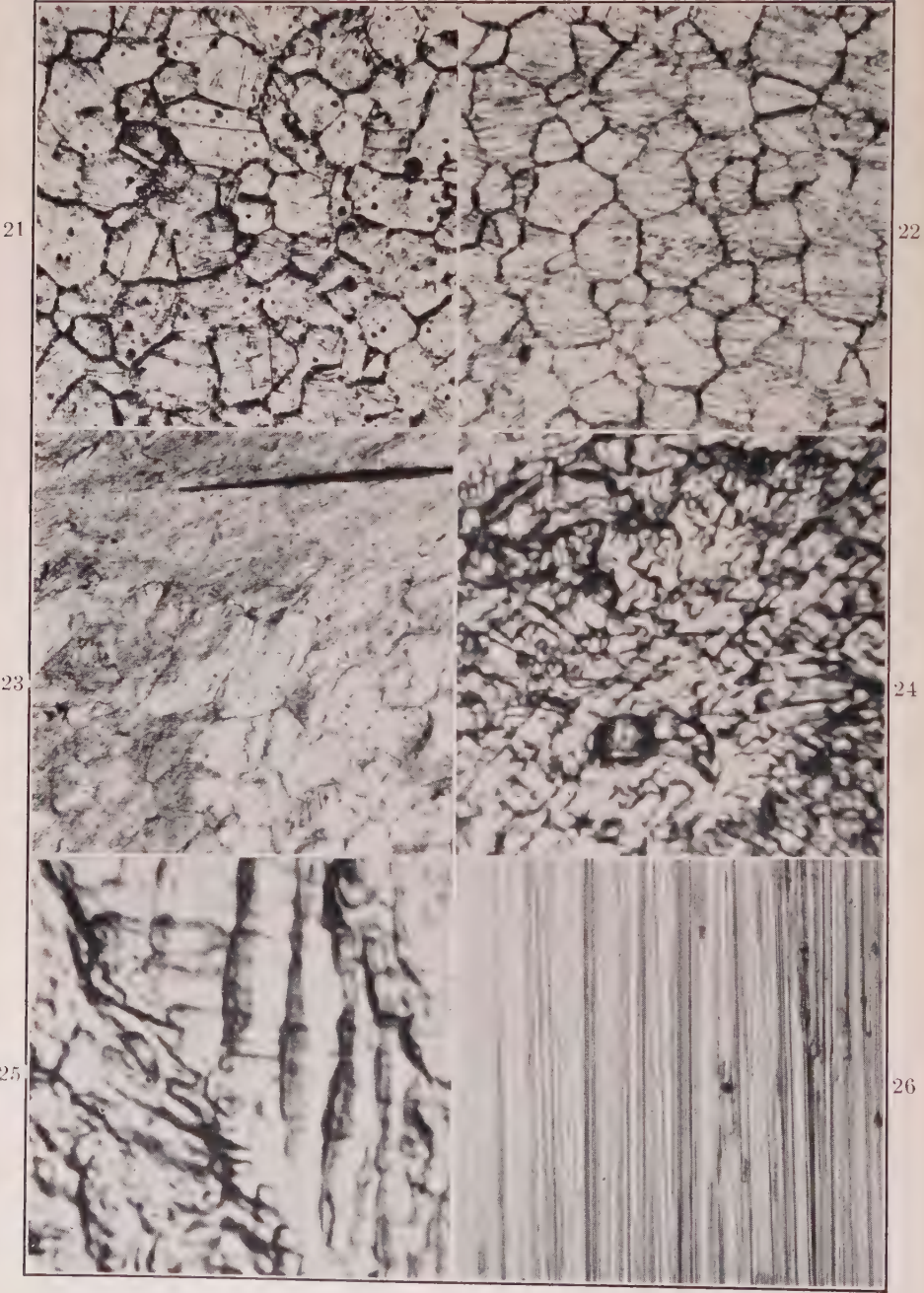
FIG. 16.—ZONE OF RECRYSTALLIZED UNITS IN HOT-DEFORMED PIECE FROM DOW INGOT. ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. $\times 250$.

FIG. 17.—PIECE OF INGOT FROM SUBLIMED CRYSTALS, COLD-DEFORMED AND HEATED TO 380°C . FOR 3 HR. ETCHED WITH CONCENTRATED NITRIC ACID. $\times 100$.

FIG. 18.—PIECE OF DOW INGOT, COLD-DEFORMED AND HEATED TO 425°C . FOR 3 HR. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 19.—PIECE OF DOW INGOT, COLD-DEFORMED AND HEATED TO 500°C . FOR 30 MIN. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 20.—THIN SHEET MAGNESIUM. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 1000$. B. & L. 1.9 MM. FLUORITE OBJ., 1.3 N. A., OIL IMM.



FIGS. 21 TO 26.

flat needs only rubbing on emery paper and damp tripoli for a few seconds to prepare it for etching. Fortunately, the uniform and pitless etching that results with so many reagents allows the scratched surface to dissolve away entirely and leave the inner structure in good relief. Continued etching may only slightly deepen the relief and yet maintain it within the focal depth of the objective.

The striated surface seen in Fig. 26 shows a longitudinal section through a piece of hot-extruded rod. This is a surface as made by filing with an ordinary 10-in. mill file. Imperfections in the metal are not entirely covered over by flowed metal since magnesium is rather brittle and chips at a free edge under a slowly moving tool.

The effect of smoothing with emery paper and moist tripoli is seen in Fig. 27. The specimen was rubbed for 30 sec. on No. 1 emery paper followed by 30 sec. rubbing on moist tripoli spread on chamois skin stretched on a small board. The tripoli had been washed by suspending for ix consecutive 1-min. periods in water before finally settling and thickening for use. The tripoli was used as a thick paste so that the specimen did not come in contact with the skin. In this print, as in the previous one, the inclusions and imperfections have not been covered over. The surface of the metal is now finely granular. The striations are fine and discontinuous.

The etching is done by a simple immersion of the specimen in the reagent until the structure is clearly developed. Fig. 28 was photographed after holding the previous surface in dilute acetic acid for 20 sec.

An elapsed time of $1\frac{1}{2}$ min. is thus adequate to finish a filed surface. The time might even be reduced if desired. The three prints showing this preparation were from the same surface but not from the identical spot on the surface.

Specimens that are finished by hand and not pressed against a rapidly moving pliable fabric do not become crowned, and give large areas in good focus. There is little annoyance from scratches when finishing this way. Magnesium pits so little in several of the reagents that it is possible to obtain good structural relief without enlarging or exaggerating the imperfections.

FIG. 21.—TRANSVERSE SECTION OF COLD-COMPRESSED HOT-EXTRUDED ROD. ETCHED WITH NITRIC AND ACETIC ACIDS. $\times 100$.

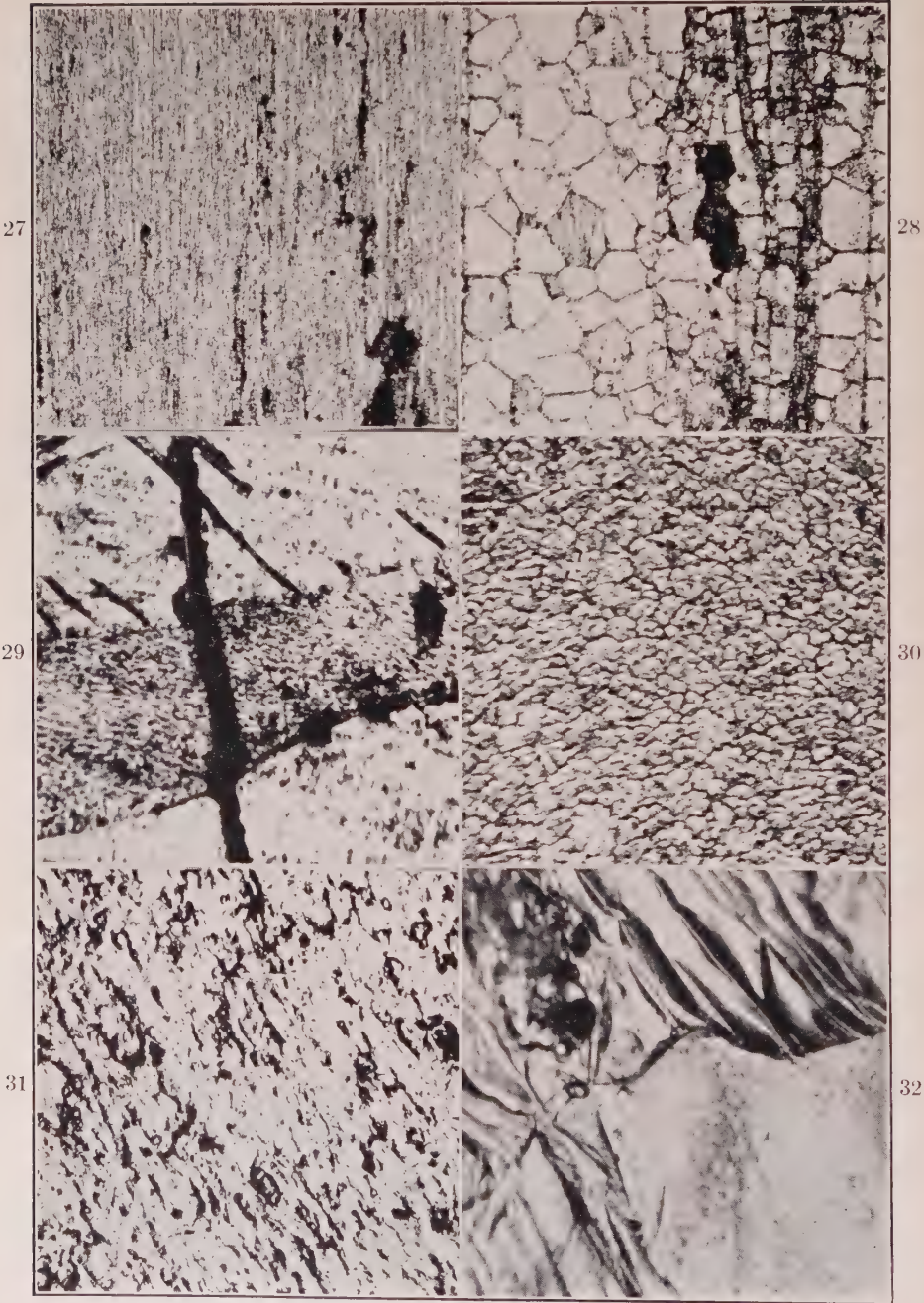
FIG. 22.—SLEDGE-STUCK (COLD), HOT-EXTRUDED ROD, TRANSVERSE SECTION. ETCHED WITH SODIUM BICARBONATE SOLUTION. $\times 100$.

FIG. 23.—FLOWED METAL IN FRACTURE ZONE OF HAMMER STRUCK, HOT-EXTRUDED ROD. ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. $\times 100$.

FIG. 24.—LAMINATIONS IN GRAIN OF HOT-EXTRUDED ROD. ETCHED WITH AMMONIUM NITRATE SOLUTION. $\times 1500$. B. & L., 1.9 MM. FLUORITE OBJ., 1.3 N. A., OIL IMM.

FIG. 25.—LAMINATIONS IN GRAIN OF HOT-EXTRUDED ROD. ETCHED WITH DILUTE ACETIC ACID. $\times 2000$. B. & L., 1.9 MM. FLUORITE OBJ., 1.3 N. A. OIL IMM.

FIG. 26.—FILED LONGITUDINAL SURFACE OF HOT-EXTRUDED ROD. UNETCHED. $\times 100$.



FIGS. 27 TO 32.

DENSITY AND HARDNESS

The specific gravity was determined by weighing pieces of from 3 to 7 gms. weight, first in air and then in water. A very fine molybdenum wire of known weight and counterpoise served for the suspension when weighing in water. It was found that gas bubbles were liberated after a few seconds, although the water was freshly boiled and cooled. A check was then run on all of the specimens, using pure carbon tetrachloride, specific gravity 1.595, instead of water. The results were the same, agreeing to one unit in the last decimal place. The true density column is corrected for the temperature (22° C.) of the water and the buoyancy of air.

The specific gravity is modified by voids, inclusions and the treatment of the metal. Although duplicate samples were run, there would be more certainty if a larger number had been averaged for each modification of the metal. Probably six samples would have been better. It is worth mentioning that, on the samples tried, the specific gravity of the cold-deformed stock was uniformly slightly less than that of the cast or annealed material. In its booklet on magnesium the American Magnesium Corp'n. states that the density of cast, extruded, rolled and annealed pure magnesium is 1.739 in all four instances. This uniformity may be open to correction on more elaborate investigation.

The scratch hardness was determined by the Bierbaum micro-character manufactured by the Spencer Lens Co. of Buffalo, N. Y. The dependence of this hardness number on the crystal orientation is evident from Fig. 29, which shows a scratch on three different units in a piece of the Dow ingot at 200 dia. magnification. The width of the scratch across the middle grain may be averaged as 0.0175 mm. and across the other two as 0.0125 mm. each. The respective hardness numbers are then 32 and 63, respectively.

The scleroscope hardness was determined with the diamond tuppet, therefore the numbers are on the standard scale. There is probably a slight loss of precision in using the scleroscope, because of the necessity of holding the specimen firmly, which may cause slight hardening through

FIG. 27.—SURFACE OF FIG. 26 AFTER RUBBING FOR 30 SEC. ON No. 1 EMERY PAPER AND 30 SEC. ON MOIST TRIPOLI HEAPED ON CHAMOIS SKIN. UNETCHED. $\times 100$.

FIG. 28.—SURFACE OF FIG. 27 AFTER ETCHING FOR 20 SEC. IN DILUTE ACETIC ACID. $\times 100$.

FIG. 29.—BIERBAUM MICROCHARACTER SCRATCH ON SECTION OF DOW INGOT. $\times 200$.

FIG. 30.—SECTION FROM FURNACE-COOLED INGOT OF MAGNESIUM-ALUMINUM (4 PER CENT.) ALLOY. ETCHED WITH DILUTE ACETIC ACID. $\times 10$.

FIG. 31.—VERTICAL-LONGITUDINAL SECTION THROUGH PLATE OF HOT-ROLLED MAGNESIUM-ALUMINUM (4 PER CENT.) ALLOY. GRAIN BOUNDARIES IN MAGNESIUM MATRIX SHOW FAINTLY. ETCHED WITH 2 PER CENT. NITRIC ACID IN ALCOHOL. $\times 100$.

FIG. 32.—SAME MATERIAL AND SECTION AS FIG. 31 BUT ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. $\times 1000$. B. & L., 1.9 MM. FLUORITE OBJ., 1.3 N. A., OIL IMM.

cold deformation. The very low elastic limit of magnesium is evident from the ease with which it slips and emits sound when squeezed even lightly. A full section from the furnace-cooled ingot from distilled crystals was cold-rolled with small reductions. The metal hardened from about 10 to over 20; the large dendrites split apart and made an interesting but worthless object.

TABLE 2.—*Density and Hardness of Magnesium*

Material	Specific Gravity	True Density	Microchar. Hard. No.	Sclero-scope
Distilled crystals,.....	1.735	1.730	25	9-11
Ingot from crystals,.....	1.742	1.737		8-12
Dow ingot,.....	1.740	1.735	25-63	11-15
Hot-extruded,.....	1.743	1.738	100	14-17
Ingot from crystals, cold-strained,...	1.741	1.736		19-22
Hot-extruded, cold-strained,.....	1.742	1.737		19-22
Dow ingot, hot-worked,.....	1.741	1.736	63	12-17
Thin sheet,.....	1.745	1.740	125	19-21
Magnesium-aluminum alloy, cast, ...	1.772	1.767	82-120	16-18
rolled plate,.....	1.772	1.767	82-120	22-23
hard particles,.....			1100	

MAGNESIUM-ALUMINUM ALLOY

The particular alloy examined had a very much finer structure in the furnace-cooled ingot than the pure magnesium. The rolled plate, however, was much coarser than the thin sheet magnesium. A section of the furnace-cooled ingot, etched with dilute acetic acid and magnified 10 dia., is shown in Fig. 30. This cast alloy has a strongly cored dendritic texture with a dark etching envelope about a white component (probably Al_2Mg_3) left in the interstices. In the hot-rolled plate the interstitial components are dispersed throughout the solid-solution matrix which has recrystallized and resembles pure magnesium in its grain characteristics. Fig. 31 is from a vertical longitudinal section of the plate after etching with 2 per cent. nitric acid and magnifying 100 dia. The grain characteristics are not very clear at this magnification. Fig. 32 is from the same surface after etching with nitric and acetic acids in acetone and magnifying 1000 dia. At this magnification the grain borders are prominent and the markings resemble those of pure magnesium. A particle of the dark component is seen in one corner of the print. This component should be the Al_2Mg_3 -Mg solid-solution eutectic, or rich in that compound, and probably containing manganese. Its hardness is about 1100 on the microcharacter scale.

ACKNOWLEDGMENTS

The microscopical work for this study was done in the Morley chemical laboratory of Western Reserve University, Cleveland, Ohio. Prof. H. S. Booth greatly facilitated the work by his active interest and cooperation.

REFERENCES

- D. HANSON and MARIE L. V. GAYLER: The Constitution of the Alloys of Aluminum and Magnesium. *Jnl. Inst. of Metals* (1920) **24**, 201.
 JOHN A. GANN and ARTHUR W. WINSTON: Magnesium and Its Alloys. *Indus. & Eng. Chem.* (1927) **19**, 1193.
 Magnesium (booklet) American Magnesium Corp., Niagara Falls, N. Y. (1923).

DISCUSSION

H. B. PULSIFER (written discussion).—Two photomicrographs (Figs. 33 and 34) illustrate conditions not fully covered in my paper. Fig. 33 shows the structure of a heavily flowed hammer-struck metal at 500 dia., after etching with acetic and nitric acids in acetone. The usual equiaxed grains are absent, certain zones appear to have

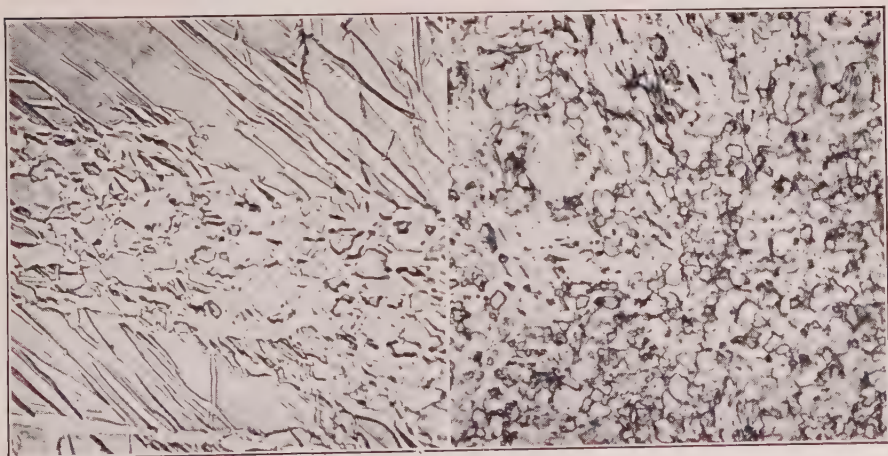


FIG. 33.—HAMMER-STRUCK INGOT MAGNESIUM. ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. NORMAL TYPE OF EQUIAXED GRAINS ABSENT. $\times 500$.

FIG. 34.—HAMMER-STRUCK INGOT MAGNESIUM HEATED TO 140°C . FOR 5 MIN. ETCHED WITH NITRIC AND ACETIC ACIDS IN ACETONE. LARGELY RECRYSTALLIZED IN TYPICAL FINE EQUIAXED GRAINS. $\times 200$.

attempted recrystallization. Fig. 34, at 200 dia., shows the same material after heating to 140°C . for 5 min. This places the recrystallization temperature of magnesium at least lower than 140°C . A limited test of the hardness gives, on the scleroscope scale, 23 for the original hammer-struck slab and approximately 21 for the recrystallized piece.

J. A. GANN, Midland, Mich. (written discussion).—Mr. Pulsifer's paper contains much valuable information, but we feel that he has created certain false impressions relative to the structure of magnesium and methods of developing it.

Specimens prepared according to his methods are better adapted for macro-structural than for microstructural examination. This is confirmed, first, by the statement on page 473, that the etching has entirely dissolved away the scratched surface, leaving the inner structure in good relief, and second, by most of his photomicrographs, which are characterized by broad crystal outlines and relief surfaces. The broad boundaries might lead one to believe that the crystals are surrounded by a more or less continuous film of impurities, whereas, with most etchants and proper technique, it is possible to develop the true hairlined crystal outlines in this pure metal. Fig. 17 shows magnesium etched with concentrated nitric acid and might be considered an exception because of its fine delineation and apparent flatness of field. Figs. 35 and 36 herewith submitted clearly show, however, that concentrated nitric acid yields considerable relief and a macro-etch.

An examination of Table 1 reveals the fact that the reagents used may be divided into two general classes:

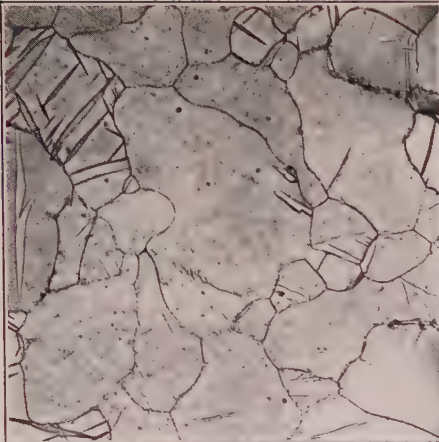
1. Pitting etchants such as acids in aqueous solution and neutral salts of the alkali metals.
2. Non-pitting etchants such as acids in nonaqueous solution, ammonium salts, and sodium carbonates.

This second group, with few exceptions, constitutes the list of recommended etching reagents. We believe, however, that the real basis for this division is not to be found in the so-called "pitting" or "non-pitting," but rather in the different character of the chemical activities of these etchants toward magnesium. Reagents in the second group are much less active than those in the first group, and dissolve the boundary in preference to the groundmass of the crystal. This is often desirable because of the bright appearance of the crystal, but may fail to reveal the whole story.

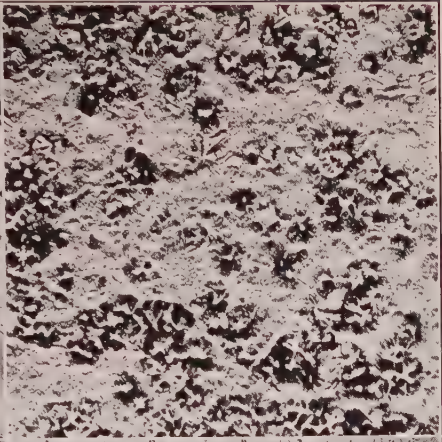
Our experience indicates that different etchants are capable of portraying greater structural differences than have been shown by Mr. Pulsifer. Fig. 37 shows the structure at 100 dia. of a chill-cast magnesium ingot, 1 in. dia., after etching 10 sec. in a 2 per cent. aqueous solution of nitric acid. The metal is composed of polyhedral grains interspersed with a number of more or less well-defined star dendrites. The ghost-line banded structure in the polyhedral grains is a remnant of the dendritic segregation of the primary crystallization. Repolishing and etching 45 sec. with a 5 per cent. aqueous solution of ammonium nitrate gives the structure shown in Fig. 38. This etching develops the same polyhedral grains traversed by the same needles, but gives no indication of the original dendritic crystallization. The cored structure of this field can be reproduced by repolishing and reetching with nitric acid or by superimposing a nitric acid etch on the ammonium nitrate etch as illustrated in Figs. 39 and 40. In Fig. 39, the nitric acid treatment was so light that a uniform etch was not obtained, while in Fig. 40, the etching was sufficient to bring out the dendritic crystallization. This dual treatment is not recommended, however, because of the tendency to deep etching. These photomicrographs have been submitted to show that this structure is inherent in this metal.

-
- FIG. 35.—CHILL-CAST MAGNESIUM. ETCHED BY PICKLING 30 SEC. IN CONCENTRATED HNO_3 . $\times 100$.
- FIG. 36.—CHILL-CAST MAGNESIUM. SAME FIELD AS FIG. 35. $\times 10$.
- FIG. 37.—CHILL-CAST MAGNESIUM. ETCHED 10 SEC. IN 2 PER CENT. HNO_3 . $\times 100$.
- FIG. 38.—CHILL-CAST MAGNESIUM. ETCHED 45 SEC. IN 5 PER CENT. NH_4NO_3 . $\times 100$.
- FIG. 39.—CHILL-CAST MAGNESIUM. ETCHED 45 SEC. IN 5 PER CENT. NH_4NO_3 PLUS 5 SEC. IN 2 PER CENT. HNO_3 . $\times 100$.
- FIG. 40.—CHILL-CAST MAGNESIUM. ETCHED 45 SEC. IN 5 PER CENT. NH_4NO_3 PLUS 10 SEC. IN 2 PER CENT. HNO_3 . $\times 100$.

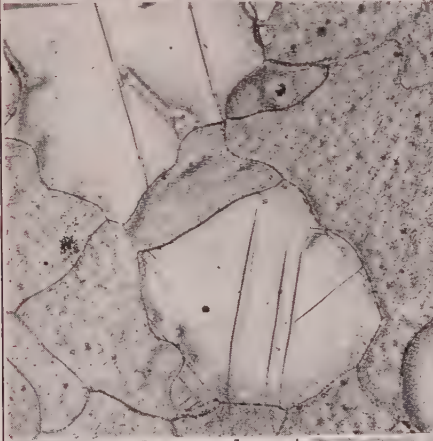
35



36



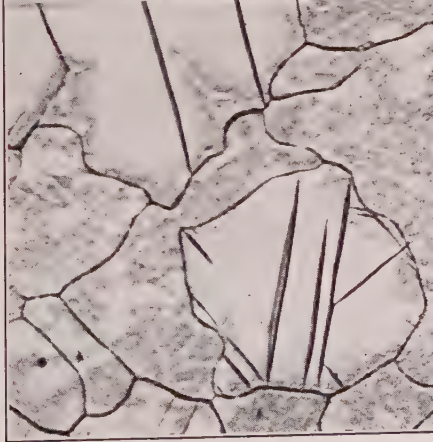
37



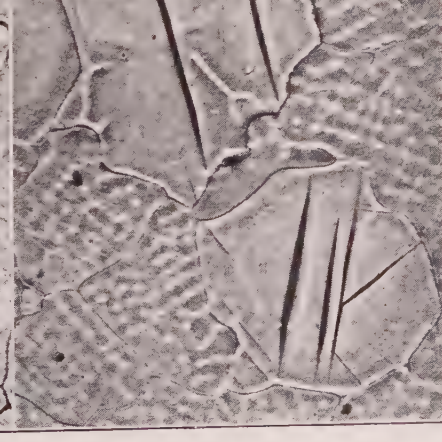
38



39



40



FIGS. 35 TO 40.

We believe that most of Mr. Pulsifer's pitting is due to a selective etching in the dendritic segregation. The ease with which this structure may be developed depends on numerous factors, including etching selectivity, rate at which the metal is cooled, and purity of the metal. Hydrochloric acid often shows a few isolated spots, which on first glance appear to be independent of the primary crystallization. Nitric acid is

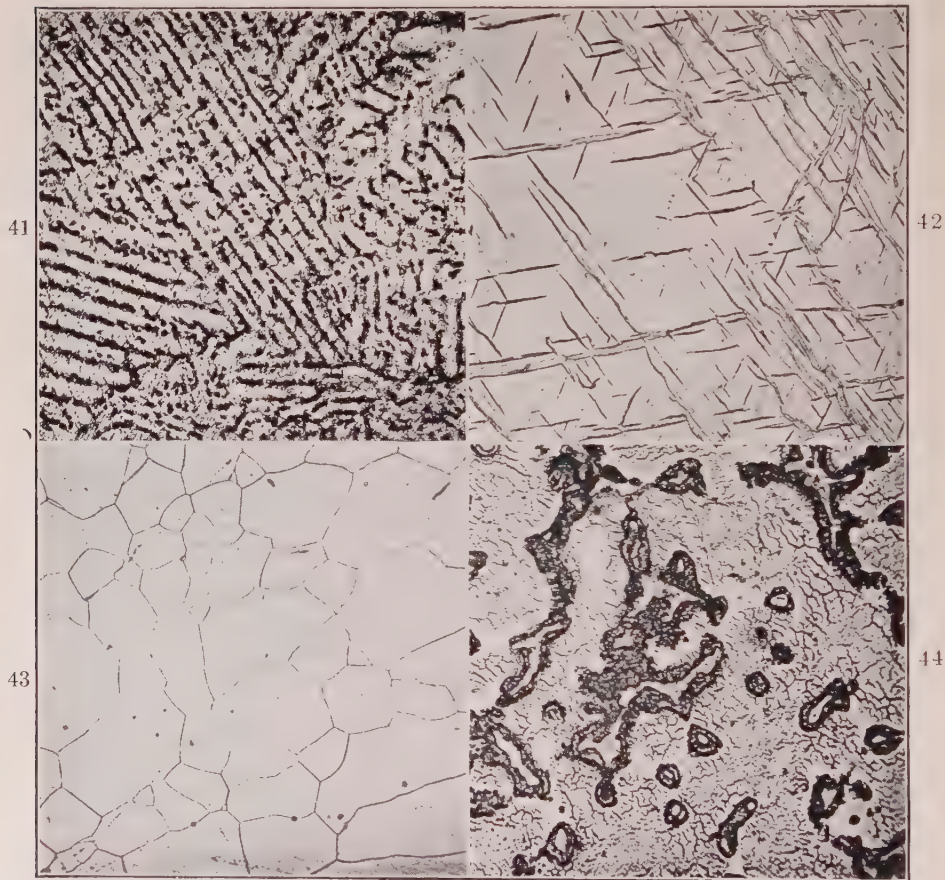


FIG. 41.—CHILL-CAST CRUDE MAGNESIUM. ETCHED 6 SEC. IN 2 PER CENT. HNO_3 . $\times 50$.

FIG. 42.—FURNACE-COOLED PURE MAGNESIUM. ETCHED 10 SEC. IN 2 PER CENT. HNO_3 . $\times 100$.

FIG. 43.—COLD-WORKED PARTLY RECRYSTALLIZED MAGNESIUM. ETCHED 10 SEC. IN 2 PER CENT. HNO_3 . $\times 200$.

FIG. 44.—SAND-CAST MAGNESIUM—8 PER CENT. ALUMINUM ALLOY. ETCHED 8 SEC. IN 2 PER CENT. HNO_3 . $\times 200$.

more selective and may reveal coring. Rapid cooling and impure metal yield a very pronounced banded structure. This is illustrated by Fig. 41, which shows a five-year old sample of crude chill-cast magnesium etched 6 sec. in 2 per cent. aqueous nitric acid. Slowly cooled pure metal similarly etched gives little to no dendritic segregation, Fig. 42. The amount of information thus obtained certainly justifies the use of nitric acid as an etchant.

The objection to nitric acid because of its tendency to stain is not warranted if proper concentrations are used. Two per cent. nitric acid has been employed in a large proportion of our work and very little difficulty experienced. This reagent is likewise capable of developing clear-cut fine detail both in the pure metal and in alloys. Fig. 43 shows recrystallized pure magnesium, which had been cold worked previously by a Brinell hardness test. Fig. 44 shows a sand-cast 8 per cent. aluminum alloy. Both structures were developed with 2 per cent. aqueous nitric acid and reproduced at 200 diameters.

Although each etchant attacks magnesium in a specific manner, the more important structural features can be developed with a single reagent by varying the technique. The three important factors that need control are time, concentration, and agitation. A relatively short etch reveals the crystal boundaries and needles, while a longer etch brings out the orientation and indications of the primary crystallization. Mr. Pulsifer's recommended reagents which we have used likewise reveal these latter details. It is obvious, however, that the time required to develop definite detail will vary with different etchants. Agitation of the specimen increases the contrast by promoting the attack of the grain boundaries. Swabbing retards the development of the cored or dendritic structure. When etching with sodium carbonate, rubbing is essential, as otherwise the specimen becomes covered with a film of basic salts that protect the metal from further attack. Increasing the concentration increases the rate of attack. With continued etching in concentrated reagents, the violent action becomes equivalent to a swabbing effect so that the etching becomes less selective and the evidences of dendritic segregation disappear. This has been observed both with acids and ammonium salts.

Most of the above comments on etching refer to pure magnesium only. Great care must be exercised in attempting to apply conclusions thus obtained to magnesium alloys. The presence of intermetallic compounds and solid solutions introduce new conditions that modify the action of the different etchants.

We have purposely refrained from applying the term "Neumann bands" to the needlelike structure so characteristic of magnesium. Certain observations have been made which support the contention that these needles are Neumann bands. First, the star dendrites referred to above occur almost exclusively in chill-cast metal where solidification stresses are greatest. These star dendrites contain more needles than the surrounding metal. Second, low-temperature recrystallization of slightly cold-worked metal containing very large needles may take place within these needles before any appreciable change in structure has occurred in the other portions of the magnesium.

Needles are present in sand-cast, chill-cast, hot-worked, and cold-worked metal. Annealing cast specimens 20 hr. at 400° C. does not decrease their number. If this structure is due to Neumanns, it means that a sudden application of stress is not required to produce them unless it be that the contractive forces during solidification are sufficient. The appearance of countless needles in a sample of very slowly solidified and cooled metal is still harder to explain. The specimen used for Fig. 42 was cut from a mass of metal cooled in a large electrically heated furnace where a cooling rate of 10° C. per hr. was maintained over the range 670° to 630° C., followed by self-cooling to room temperature during an additional 40 hr. In contradistinction to the apparent ease with which certain needles are formed, we have found that quickly applied force does not always increase the number of needles originally present.

The only magnesium wherein we have not observed needles is metal recrystallized after strenuous cold working. Needles have been seen in partly recrystallized magnesium, but they were so large and so situated with reference to the original dendritic structure that we feel they were remnants of the primary crystallization. Two of Mr. Pulsifer's photomicrographs, Figs. 17 and 18, show cold-worked and

subsequently heated magnesium containing these needles. Perhaps the cold working was insufficient to secure maximum grain refinement on recrystallization.

While these needles possess many of the characteristics of Neumann bands, a number of observations have been made that are not entirely consistent with the general conception of the term.

A. J. PHILLIPS, Waterbury, Conn.—Mr. Pulsifer says, "The Neumann markings occur frequently in all the specimens examined. There was no hint that resurfacing caused more markings to develop or that the surfacing operations caused those that were found."

Fig. 18 shows a structure that we have commonly found in magnesium. It may easily be developed if the last stage of polishing is not carried far enough. When a specimen is polished on coarse emery, structural deformations are brought about on the surface layers which a superficial polish with flour emery will not remove. Upon etching these deformations are manifested by streaks resembling scratches but which consist of thousands of short parallel etch markings. Fig. 19 shows a hint of them but in this case the final polishing has evidently gone far enough to remove them to a considerable extent.

It is possible to develop similar markings and, in fact, it is impossible to avoid their development in coarse-grained specimens of pure zinc and cadmium unless considerable time is spent in the final polishing stage, for they are formed in these metals upon very moderate abrasion.

Mr. Pulsifer refers to the markings as Neumann bands. In the paper on Twinning in Beryllium, Magnesium, Zinc and Cadmium,¹ it was demonstrated that the structural markings in magnesium occupy planes of form $\{1012\}$ of the hexagonal close-packed lattice having an axial ratio of 1.62. From the similarity of these bands to mechanical twin bands in zinc it was concluded that they were also mechanical twins, a name which is perhaps a trifle more descriptive than Neumann bands.

I can substantiate Mr. Gann's statement that shock is not necessary to form these twins for I have often formed them by slowly squeezing a specimen of coarse-grained magnesium in a vise. The general dimensions and extent of the bands depends both on the purity of the element employed and the method of straining the specimen. For instance, quenching a heated specimen usually produces quite long scattered twin bands while polishing will produce bands as short as the width of a scratch and so fine and closely packed that they can be resolved only at very high magnifications.

It is interesting to note that Beilby, in his development of his amorphous theory, called attention to the fact that if large scratches are developed on the surface in polishing calcite, antimony or bismuth, these scratches disappear upon continued polishing with finer emery but apparently reappear upon etching. It was his theory that the flowing of the surface in the form of amorphous material covered up the scratches while etching dissolved off this amorphous surface and exposed underlying scratches. Since it has been amply demonstrated by E. Reusch and O. Mügge that calcite, antimony and bismuth twin mechanically with great ease, it is probable that Beilby's alleged scratches were really rows of exceedingly fine parallel twin bands. I have often unintentionally succeeded in preparing specimens of zinc that were quite deceiving in this respect.

H. B. PULSIFER.—There is one point which Mr. Gann brought out about the rays in the quenched material. I have seen those and they were so startling I did not want to make any slides and bring them to show to you, but what he said I believe is perfectly correct.

¹ See page 445.

Manganese in Non-ferrous Alloys

BY M. G. CORSON,* NEW YORK, N. Y.

(Cleveland Meeting, April, 1927)

INFORMATION regarding the use of manganese alloys has hitherto been incomplete and available only from widely scattered sources. This paper attempts a systematic description of properties and uses of alloys other than manganese bronze, manganin and duralumin, which are probably the only non-ferrous alloys associated with manganese in the minds of most metallurgists.¹

PROPERTIES OF MANGANESE

Manganese can react either acid or basic; it is hard to obtain in the pure state; it has two different crystalline lattice structures, both of the cubic system, one stable above 850° C. and the other below 650° C., both coexisting in the intermediate range. Although the commercial product is hard and brittle, the pure metal seems to be ductile. In fact Zhemchuzhny, in Russia, was able to obtain ductile manganese and draw it to fine wires by the simple expedient of adding about 3 per cent. copper to the aluminothermic product. Copper most probably brings the silicides, aluminides, nitrides and carbides present in the commercial product into a much less harmful form of distribution.

One industrial use that can be foreseen for wrought manganese articles is as anodes for electrolytic processes in sulfate and nitrate solutions, particularly with high voltages. A practically insoluble skin of manganese peroxide is likely to form in such cases and an insoluble and strong anode material will be available.

MANGANESE AS A SCAVENGER

Because of its activity manganese might become the most efficient scavenger and refiner of copper, were it not for the fact that 0.01 per cent.

* Consulting engineer.

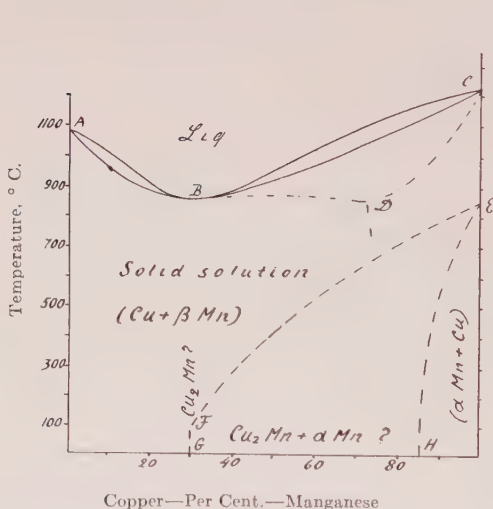
¹For studies of the crystalline structure of manganese during the last 5 years, see A. Westgren and G. Phragmen: *Zum Kristallbau des Mangans. Zeitschr. Physik* (1925) **33**, 777; and A. J. Bradley: *The Allotropy of Manganese. Phil. Mag.* (1925) **50**, 1018.

of manganese remaining in solid solution will reduce the electric conductivity of copper by 2.2 per cent. Nevertheless, the use of manganese for this purpose is possible. The writer made some laboratory tests in which he was able to eliminate oxygen without affecting conductivity.

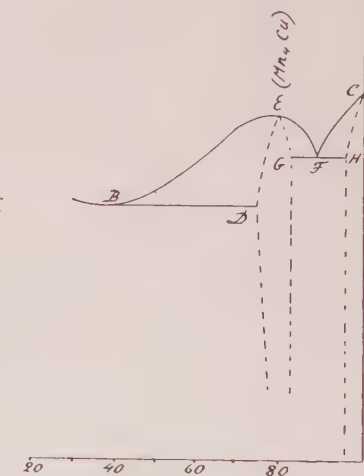
Manganese is also likely to combine with the traces of sulfur and, by removing these two impurities, it immediately brings the ductility and strength of cast copper to the inherent values of the pure metal ($32,500 \pm 1,500$ lb. and 65 ± 5 per cent. elongation in 2 in.).

THE BINARY SERIES COPPER-MANGANESE

Two independent investigators, Sahmen and Zhemchuzhny, working about the same time, came to the conclusion that the binary series copper-



Copper—Per Cent.—Manganese
Fig. 1a.



Copper—Per Cent.—Manganese
Fig. 1b.

FIG. 1a.—CONSTITUTIONAL DIAGRAM OF THE CU-MN SERIES.

ABC, Incipient and complete melting point curves according to Zhemchuzhny. *BDC*, Complete solidification curve for high-manganese alloys as traced by Sahmen, but considered by him not to correspond to actual conditions. *EF*, Hypothetical curve of the transformation of beta-manganese to alpha as affected by the presence of copper. *FG*, Hypothetical change of a 30 per cent. manganese alloy into a MnCu_2 compound of the same crystalline type with copper.

FIG. 1b.—VARIANT OF THE CONSTITUTIONAL DIAGRAM IN THE HIGH-MANGANESE RANGE AS FOUND BY VOLOGDINE IN 1907 (BEFORE ZHEMCHUZHNY'S INVESTIGATION).

manganese is an example of continuous solid solubility, that is, both metals can substitute one for the other in their specific crystalline lattices atom for atom without any limitation. This is the essence of the equilibrium diagram as established by Zhemchuzhny (Fig. 1a, the heavy line).

The data of Zhemchuzhny,² Sahmen³ and Wologdine⁴ agree on the copper end of the diagram but not on the manganese-rich side. Under these circumstances it seems very strange that the scientific world accepted Zhemchuzhny's conclusions without retesting them for 18 years.

Among the noticeably few studies of the equilibrium diagram and microscopic structure of the copper-manganese series are those of Bain⁵ and Patterson,⁶ who concluded that up to 30 per cent. manganese the alloys actually form a perfect solid solution, and beginning at this point, another constituent appears and increases in importance to about 90 per cent. manganese when it becomes the only constituent present.

The fact that manganese is allotropic also militates against accepting high-manganese alloys as representing single solid solutions. Granted that beta manganese, the form stable above 850° C., is identical in crystal-line structure with copper, the temperature of its allotropic change must be considerably shifted by the presence of copper and the change is bound to introduce the disintegration of the single phase, stable at higher temperatures, into a mixture of two separate phases. This is represented hypothetically by the dotted lines *GFEH* in Fig. 1*a*.

PHYSICAL PROPERTIES AND INDUSTRIAL USES

When some manganese is left in solid solution, all properties of the copper change in a strictly continuous way, at least up to 30 per cent. manganese.

All copper-manganese alloys, up to 30 per cent., can be made satisfactorily in a furnace of any kind. Those made on a basic bottom and fully protected from the action of the fuel gases will have considerably higher ductility than those made in graphite or fireclay crucibles, as they absorb carbon in proportion to the manganese content. The former will show 60 ± 5 per cent. elongation in 2 in. in the wrought and annealed state; the latter may not show more than 40 ± 5 per cent. At 30 per cent. manganese as much as 0.20 per cent. carbon may be expected in an alloy made in a graphite crucible and stirred with a graphite bar. A continuous contact with charcoal will cause an absorption of about 0.5 per cent. C, the alloys becoming cold short (biscuit structure). Reasonably pure alloys (below 0.1 per cent. carbon) roll well either hot or cold and draw just as well. Alloys containing up to 0.15 per cent. carbon cold

² S. Zhemchuzhny, G. Urasow and A. Rykowski: Legierungen des Mangans mit Kupfer und Nickel. *Zeitschr. anorg. Chem.* (1908) **57**, 253.

³ R. Sahmen: Über die Legierungen des Kupfers mit Kobalt, Eisen, Mangan und Magnesium. *Zeitschr. anorg. Chem.* (1908), **57**, 1.

⁴ S. Wologdine: Alliges de Manganese et de Curve. *Rev. de Met.* (1907) **4**, 25.

⁵ E. C. Bain: Crystal Structure of Solid Solutions. *Trans.* (1923) **68**, 625.

⁶ R. Patterson: Crystal Structure of Copper Manganese Alloys. (Abstr.) *Phys. Rev.* (1924) **23**, 552.

roll well but do not stand heavy drawing. For cold rolling, 0.1 per cent. carbon should be considered as the maximum permissible.

Hardness

The Brinell values for the binary series were independently studied by Wologdine,⁷ Norbury,⁸ Zhemchuzhny⁹ and the author. It is not so easy to reconcile the various data as variations are caused by not taking the influence of carbon into consideration. Even as little as 0.05 per cent. carbon may cause the formation of 0.7 per cent. of Mn_3C , which

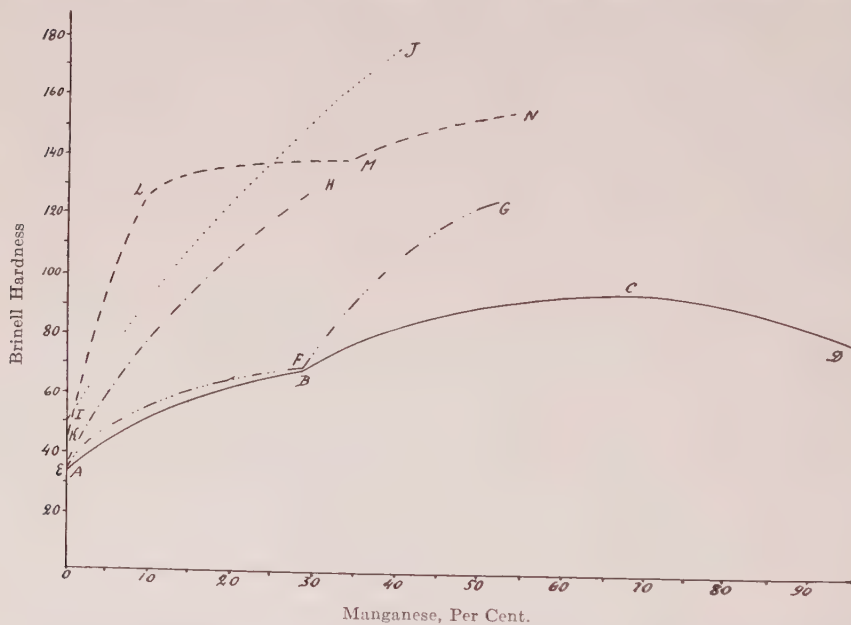


FIG. 2.—BRINELL HARDNESS OF THE CU-MN SERIES.

ABCD, Hardness of wrought and annealed alloys of high purity (Zhemchuzhny) *AFG*, Hardness of rolled and thoroughly annealed alloys made in a graphite crucible on a large scale (Corson). *EHI*, Hardness of forged annealed alloys according to Norbury. *IJ*, Hardness of cast and annealed specimens according to Vologdine (made in a gas furnace and clay crucibles). *KLMN*, Hardness of rolled alloys, quenched from 800° C. and drawn at 450° C. (Corson).

may affect the hardness considerably should it happen to be present in a state of ultra-microscopical dispersion. This state is easily produced by quenching a rolled alloy from 800° C. and drawing at 400° to 450° for 24 hr. Very slow cooling causes the carbide to coalesce and the hardness becomes more nearly normal. Curve *A-B-C-D*, Fig. 2, represents the hardness of thoroughly annealed alloys according to Zhemchuzhny and

⁷ S. Wologdine: *Op. cit.*

⁸ A. L. Norbury: The Hardness of Certain Copper α Solid Solutions. *Jnl. Inst. Met.* (1923) **29**, 423.

⁹ S. Zhemchuzhny: *Op. cit.*

was fairly well corroborated by the author's experiments (Curve *AFG*). Curve *KLMN* represents the hardness of the quenched and drawn alloys (with not over 0.15 per cent. carbon at 30 per cent. manganese). Brinell hardness of 67 is fairly representative for the pure alloy of the minimum melting point, just as it is for the saturated wrought and annealed tin bronze, aluminum bronze and silicon bronze. The hardening effect of manganese is small in the beginning, develops the maximum effect per

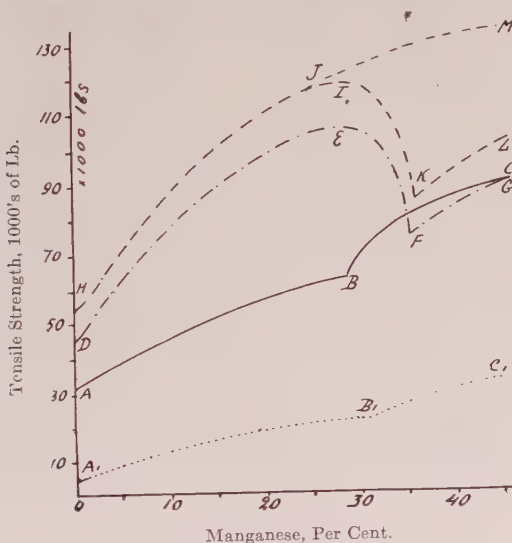


FIG. 3.—*ABC* TENSILE STRENGTH OF ROLLED AND ANNEALED ALLOYS MADE ON A LARGE SCALE. THE ELONGATION IN 2 IN. DID NOT GO BELOW 50 PER CENT. IN THE RANGE *AB* NOR BELOW 35 PER CENT. IN THE RANGE *BC* (CORSON).

A₁B₁C₁, Yield point (0.5 per cent. elongation in 2 in.) of the rolled and annealed 750° C. alloys (Corson). *DEFG*, Strength of alloys quenched from 800° and cold-rolled to 50 per cent. reduction (Corson). *HJKL*, Strength of alloys cold-rolled 75 per cent. (Corson). *EFG* and *IKL* are believed to represent the decrease in strength due to internal cracks caused by carbide precipitation. For carbon and silicon-free alloys a 75 per cent. reduction would probably result in the curve *HJM* for ultimate tensile strength.

unit at about 0.5 per cent. manganese and slows down to approximately 0.7 Brinell unit per 1 per cent. at 30 per cent. manganese. The sharp break (*B*, *F*) near 30 per cent. and the further increase in hardness beyond the minimum point might be explained either by the increase in carbon content or the formation of a compound Cu_2Mn .

Strength

The strength of Cu-Mn alloys runs largely parallel to their Brinell hardness (Fig. 3.). At 30 per cent. manganese the wrought and annealed alloy reaches the strength of $63,000 \pm 3000$ lb. Quenching from 830° C. brings it up to 70,000 lb.

Cold rolling brings the hardness of the alloy at minimum melting point to 190 Brinell and its strength to $120,000 \pm 5000$ lb., which figures are also representative for all saturated and hard-rolled solid solution alloys of copper base.

The *scleroscopic hardness* of the minimum melting point alloy varies between 18 (universal hammer), as soft annealed, and 43 as cold-rolled, which also corresponds to the general properties of copper alloys. In the presence of a slight amount of carbon, one may obtain a scleroscopic hardness of 25 by quenching from 800°C .

VALUABLE PROPERTIES OF COPPER-MANGANESE ALLOYS

So far no specific properties of the copper-manganese alloys have been mentioned that might make them more satisfactory than other alloys from the viewpoint of the engineer. Manganese shifts the annealing point of copper just as definitely upward as nickel, but it takes less manganese than nickel to raise the point of the incipient anneal to the same level. This, coupled with a greater hardening effect per unit added, makes copper-manganese alloys a desirable material for steam turbine blades working in moderate temperature ranges.

The question arises as to where to stop the addition of manganese in the manufacture of turbine blade stock. Requirements of strength taken alone would indicate the minimum point alloy with its 400°C . of incipient anneal as the best choice. The requirement of good brazing qualities make it imperative however to drop the manganese content considerably and the requirement of a good resistance to the corrosive action of super-heated steam necessitates a change in the same direction. It may be questioned whether the best composition was found as the result of systematic experimentation; the present-day practice stops, however, at 5 per cent. manganese.

Another field of copper-manganese applications is in the construction of locomotive fire-box plates and stays. The presence of manganese makes these parts immune to the effects of alternative oxidation and reduction caused by the flames changing from an oxygen to a carbon-monoxide rich condition, and just as well to the action of sulfur dioxide, which is easily absorbed by pure copper and its ordinary alloys. In this latter application the European and particularly the English practice stops arbitrarily at 4 per cent. manganese.

Electrical Features of the Copper-manganese Series

The considerable increase in the electrical resistivity of copper brought about by an addition of manganese was noticed long before even the solid solution nature of these alloys became established; *manganin*, as well as *resistin*, both copper-manganese alloys, came into use about 35 years ago in the construction of resistance coils and were practically the first

materials of a constant resistivity. From that time on four independent investigations of the electrical conductivity of the binary series¹⁰ were made, one of them including alloys containing as much as 97 per cent. manganese. Inasmuch as small amounts of carbon and silicon do not rob the groundmass of the alloy of much manganese, the electric resistance data of all authorities agree pretty well.

The resistivity of copper-manganese alloys increases along a slightly convex curve (Fig. 4) up to 40 per cent. manganese where the resistivity-composition ratio decreases and the curve, of an approximately hyperbolic

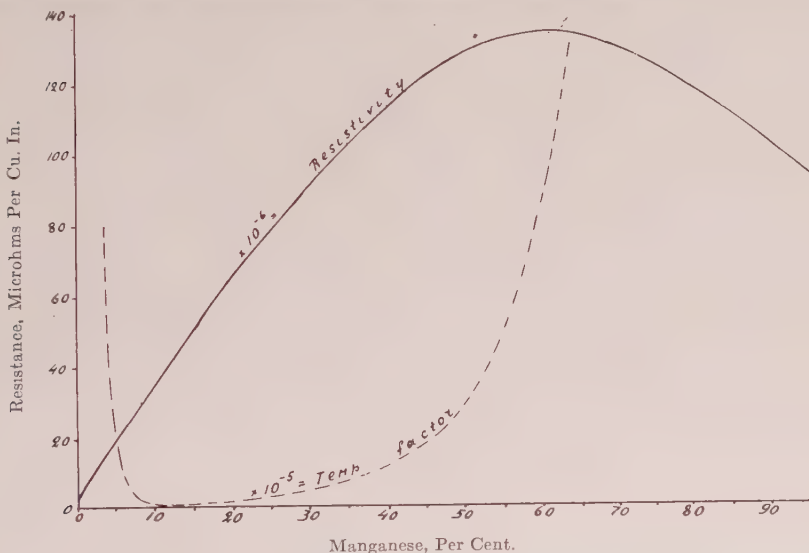


FIG. 4.—ELECTRIC PROPERTIES OF THE CU-MN SERIES (ZHEMCHUZHNY).

type, reaches a maximum of 138 microhms per cu. cm. at 60 per cent. manganese. There is accordingly a rather wide range of compositions to choose from when considering high resistivity alone.

The desirable range for resistance wires is narrowed as is evident from the shape of the curve showing the temperature coefficient of resistivity of the series. The minimum temperature coefficient, of the order of two millionth parts per degree Centigrade, lies between 12 and 17 per cent.

¹⁰ K. Feussner and S. Lindeck: Die elektrischen normal-Drahtwider-Stände der Physikalisch-Technischen Reichsanstalt. Berlin, *Phys. Reichsanst. Abh.* 2. (1895) **2**, 501.

F. M. Sebast and G. L. Gray: Electrical Resistances and Temperature Coefficients of Nickel-copper-chromium and of Nickel-copper-manganese Alloys. *Trans. Am. Electrochem. Soc.* (1916) **25**, 569.

Zhemchuzhny: *Op. cit.*

Corson (not published).

A. L. Norbury: Note on the Effects of Certain Elements on the Electrical Resistivity of Copper. *Jnl. Inst. Met.* (1925) **33**, 91.

manganese, in other words it corresponds to neither the minimum melting point nor the maximum of resistivity. It becomes imperative, therefore, to stop somewhere within the range of 45 to 70 microhms inasmuch as the most important prerequisite of a good resistance alloy is a low temperature coefficient of resistivity.

The next most important property of a good resistance material is its resistance to oxidation and tarnishing, which are apt to reduce the active section of a fine wire considerably. Now it so happens that copper is unable to extend its protective action, even at normal temperatures, beyond 12 to 14 per cent. manganese which in practice reduces the suitable range to a rather definite composition. Slight variations of an advantageous nature are introduced by the presence of nickel which is usually added in amounts up to 4 per cent.

Other advantageous features of copper-manganese alloys as resistance materials are: (a) The decrease of the temperature coefficient with the temperature until it becomes strictly zero at 45° C. Certain additions (according to Bash) shift this point down to 30° and make the alloys still more suitable for ordinary use.

(b) The practical absence of any thermoelectric phenomena at the joints of manganin wires with copper terminals—a property eliminating any disturbing currents and making manganin the best resistance material for the most delicate electric measurements.¹¹

Properties Beyond the Minimum Melting-point Composition

It is usually believed that high-manganese alloys are brittle and this opinion persists in spite of the fact that Hunter was able to roll and draw wire (from small ingots) containing up to 60 per cent. manganese and Zhemchuzhny succeeded in doing the same up to 97 per cent. Mn. The author, while associated with the Union Carbide and Carbon Research Laboratories, experimented with the manufacture of rolled alloys up to 60 per cent. on a scale and in a manner more or less duplicating plant conditions. It was found that good rollable ingots can be obtained even if the melting is done in a plain graphite crucible and in an atmosphere of carbon monoxide (carbon plate resistor furnace) if a thin cover of a protective flux (borax + soda + sodium fluoride) is used. This flux is made viscous just before pouring by adding sand or magnesia and the melt is poured into an ordinary cast-iron mold.

The rough ingots cannot be rolled successfully if the procedure suitable for rolling brass is used. The author found it necessary to start with a

¹¹ S. Kimura and K. Sakamaki: Electrical Resistivity and Its Temperature Coefficient of Manganin. *Jnl. El. Lab. Japan. Rep.* 114 (1922).

M. A. Hunter and J. W. Bacon: Manganin. *Jnl. Am. Electrochem. Soc.* (1919) 36, 323.

F. E. Bash: Manufacture and Electrical Properties of Manganin. *Trans.* (1920) 64, 261.

careful cold rolling reducing the ingot about 10 per cent. in 20 passes and annealing the stock in a muffle at $800^{\circ}\text{C}.$ for 2 to 3 hr. At this stage the material is ready for hot rolling, which can be pushed as far as desired until the material can be finished by cold rolling. With alloys containing below 0.05 per cent. carbon, the final cold rolling can be done without special precautions and pushed to 75 per cent. reduction. Above 0.05 per cent. carbon, the stock must be quenched from $800^{\circ}\text{C}.$ to keep the maximum amount of carbon in solid solution, otherwise internal cracks will occur after a cold reduction of 20 per cent. and the strength may drop even below that of the annealed material. (See curves *EFG* and *IKL* in Fig. 3.)

Again the question may be asked as to what good and profitable uses could the wrought alloys above 30 per cent. and to about 55 per cent. manganese be put? The author assumed in this connection that within the range of 37 to 63 atomic (31 to 59 by weight) per cent. of manganese, the latter might begin to exercise a protective action against oxidation by forming a skin or film of dioxide while the copper might still retain its protective power against a strictly substitutive attack by highly ionized acid solutions.

Actual experiments, although too few to be conclusive, seem to corroborate this hypothetical assumption, at least to some extent. An alloy with 48 per cent. manganese does not resist hot 10 per cent. hydrochloric acid but resists well the action of hot ($70^{\circ}\text{C}.$) 20 per cent. sulfuric acid, particularly when chromic acid is present. It would therefore be rather interesting to find out if pickling and other chemical equipment could not be manufactured from alloys of this range.

The description of the binary series would not be complete without mentioning that the low melting point of the alloys from 20 to 35 per cent. manganese and the strong but chemically neutral skin of oxide covering the surface of the molten alloy might make them suitable for die casting. The first feature would serve to prolong the life of the dies and the second to protect them from the burning in of the molten metal. Chill-cast alloys of this range are fairly uniform from the boundaries to the cores of the individual grains and possess a considerable hardness and impact resistance.

Figs. 7 to 16 show the structures of copper-manganese binary alloys of different content and after different treatments.

TERNARY COPPER ALLOYS CONTAINING MANGANESE

The study of the actual or probable properties of ternary copper-manganese alloys can be subdivided into three parts, namely:

1. The influence of manganese upon the solid solubility limits of alpha type alloys at high and low temperatures (Standard brass, cupro-nickel, coinage bronze, cold workable aluminum bronze).

2. The maximum amount of manganese that will not introduce any undesirable brittle constituents into the usual industrial alloys of a duplex structure. (Muntz metal, gun metal, 10 per cent. aluminum bronze.)

3. The influence of manganese upon beta alloys, particularly high-zinc brass (40–50 per cent. zinc).

An alpha copper-zinc alloy, for instance, the regular cartridge brass, is undoubtedly apt to absorb considerable amounts of manganese without developing a duplex structure. Metallographically, manganese seems to act very much like a substitute for copper, so there is no doubt whatsoever that an alloy with 10 per cent. manganese and 30 per cent. zinc will show

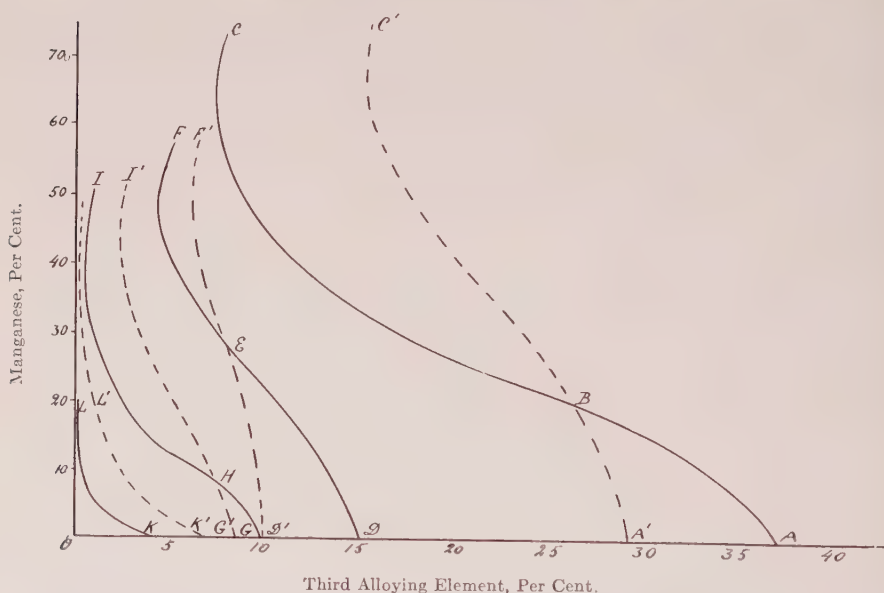


FIG. 5.—HYPOTHETICAL RANGES OF SOLID SOLUBILITY IN TERNARY COPPER-MANGANESE ALLOYS AT ROOM TEMPERATURES (HEAVY LINES) AND ABOUT 800° C. (DOTTED LINES). ABC and A_1BC_1 for Cu-Mn-Zn, DEF and D_1EF_1 for Cu-Mn-Sn, GHI and G_1HI_1 for Cu-Mn-Al, KL and K_1L_1 for Cu-Mn-Si.

in general the mechanical features of cartridge brass, probably with an increase in the ultimate strength and the elastic limit. A 20 per cent. manganese, 20 per cent. zinc alloy is also very likely to represent a variation of a 20 per cent. zinc brass and to be analogous to a 20 per cent. nickel, 20 per cent. zinc-nickel silver.

On the other hand it is quite improbable that an alloy with say 30 per cent. manganese and 25 per cent. zinc might also represent an alpha solid solution as should be the case if manganese acted simply as a substitute for copper. Some kind of an obscure law exists, according to which the wide range solid solution series, like those of copper-manganese (also cop-

per-nickel), possess a minimum solvent power for a third element at some definite ratio between the two principal metals. And though experimental proofs are not yet sufficiently established one may imagine a group of curves showing the amount of the third element soluble in binary copper-manganese alloys at various temperatures.

Fig. 5 shows a few such hypothetical "solubility lines" drawn by the author so as to present the possible behavior of the copper-manganese series toward zinc, tin, aluminum and silicon, respectively.

Usually such solubility lines are more concave at room temperatures and much less so somewhere just below the complete solidification point. This causes the alpha range to widen with an increase in temperature and creates an opportunity to harden the alloy by a combination of a quenching and a drawing process.

No experimental material is available with which to indicate even approximately those compositions in the Cu-Mn-Zn or the Cu-Mn-Sn systems where an amenability to heat hardening of this kind becomes possible. It is, however, very probable that an alloy with 35 per cent. manganese and 15 per cent. zinc or 5 per cent. tin, for example, will come within this range.

The situation is much more definite for the copper-manganese-aluminum and copper-manganese-silicon series. An alloy containing 10 per cent. manganese and 4 per cent. aluminum does not harden at all, but one with 15 per cent. manganese and 5 per cent. aluminum may be hardened to a considerable extent (160 Brinell). In the copper-manganese-silicon series an alloy with 8 per cent. manganese and 2.5 per cent. silicon may be hardened up to 100,000 sq. in. strength, 70,000 lb. per sq. in. yield point, 175 Brinell and 15 per cent. elongation, *i.e.*, it shows nearly the same mechanical features as a Corson alloy with 2.5 per cent. nickel and 0.6 per cent. silicon. It possesses, however, a greatly inferior conductivity, due to the large amount of manganese and silicon remaining in solid solution (4 per cent. manganese + 1.5 per cent. silicon do not render the alloy amenable to heat-treatment).

Manganese Bronzes

When manganese is added to a duplex (alpha plus beta) copper alloy it may (just like any other third addition) either join the phases already existing and partake in this manner in the building up of the two different crystalline lattices (ternary alpha and ternary beta) or it may form a separate phase consisting of a compound or a solid solution of some kind. As the formation of a copper-manganese compound is practically impossible and the formation of such compounds as manganese-zinc or manganese-tin is highly improbable with small amounts of manganese present, the main question is whether manganese will enter either into one of the exist-

ing alpha and beta solutions exclusively, or into both of them, and how their properties will be affected.

For the duplex brasses, the most important industrial alloys, where the presence of manganese results in the highly valuable "manganese bronzes," we find the following situation. (Fig. 6). A brass with 38 per cent. zinc and 1 per cent. manganese is just beyond the saturated alpha phase of the binary brasses (37 per cent. Zn) and is represented by the point *C* in our diagram. It is quite possible that all manganese will, in this case, go into the alpha phase. Then the ternary alpha will be represented by a point *D* located on the straight line *BC* at some distance to the left of the point *C*.

It is just as possible that a brass with 45 per cent. zinc and 1 per cent. manganese, represented by the point *F* and located just beyond the cop-

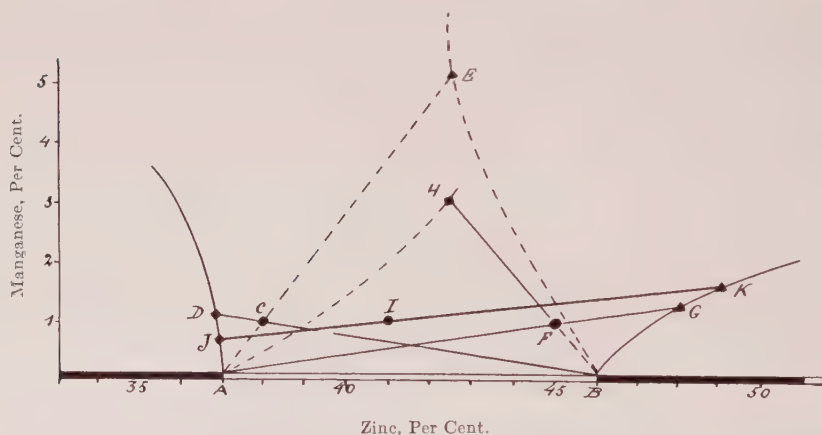


FIG. 6.—GRAPHICAL PRESENTATION OF MANGANESE DISTRIBUTION PROBABILITIES IN MANGANESE-BEARING DUPLEX BRASSES.

per-saturated beta phase, may contain all its manganese in the beta phase. The ternary beta will then be represented by the point *G* on the straight line *AF* somewhere to the right of *F*.

But it is highly improbable that all manganese of the first brass might go in the beta as represented by the point *E* on the straight line *AC*, nor might it go entirely in the alpha in the second case as represented by the point *H* on the straight line *BF*. So we come to the conclusion that in the absence of a third specifically manganese-carrying phase, the manganese of a ternary brass must be distributed in some way between the alpha and the beta phases.

If heat tinting is applied under identical conditions to a binary duplex brass, for example one with 41 per cent. zinc, and to a complex one about 41 per cent. Zn and 1 per cent. Mn, the second tarnishes and discolours pronouncedly and the microscope traces the strongest tint to the man-

ganese-containing beta phase of the second brass. The distribution factor is accordingly definitely in favor of the beta phase. This condition is illustrated by the distribution line *J-I-K* where *J* represents the low manganese ternary alpha, *K* the high-manganese ternary beta, and *I* the bulk composition of a three component duplex brass.

All of the manganese entering the alpha phase probably remains attached to it in a stable manner. The rigidity of the manganese-bearing alpha may be increased over that of the pure alpha; the total improvement obtainable in this way cannot be sufficient to warrant the manufacture of a new alloy and much less to explain the high strength of the so-called "manganese bronzes."

The manganese content of the beta phase of brasses undoubtedly represents a factor affected by the temperature, unless it is very small. The very fact that beta brass is always unsaturated and at higher temperatures easily dissolves additional amounts of either copper or zinc, makes it probable that the amount of manganese (or of any other metallic element that is likely to dissolve in the beta phase), increases with the temperature. At the temperature where the beta phase is just crystallized from the molten state, one may expect it to contain considerable amounts of manganese in solid solution. There is plenty of experimental evidence to show that a 42 per cent. zinc brass with 2 per cent. manganese represents a uniform solid solution at a temperature of say 850°. On cooling, this solid solution is bound to precipitate a good deal of the alpha phase and very probably a certain amount of manganese as well. Part of this latter goes to the larger secondary grains of the alpha phase but another part might stay as a finely dispersed Mn-Zn compound within the grain boundaries of the original beta phase. It seems probable also, that at the usual rate of cooling taking place in a casting or forging exposed to air, the manganese remains in a state of submicroscopical distribution, thus considerably increasing the strength of the beta phase. This was proved by the author in a 46 per cent. zinc brass containing 2 per cent. manganese. As cast, it had the hardness of 120 Brinell, which dropped, however, to 85 Brinell when the sample was slowly cooled in the furnace.

The usual manganese bronze does not, however, represent a ternary copper-zinc-manganese brass by any means. Elements, such as aluminum, tin, iron, sometimes nickel, enter the commercial manganese bronzes in considerable amounts, never less than 0.5 per cent. Each of these has its specific action, but at this point we are interested only in the combined effects of either tin or aluminum with the manganese. Considering the accumulated facts regarding the strength relationships in manganese bronzes, we cannot fail to come to the conclusion that formation of a compound such as MnAl or Mn₂Sn, dispersed in the beta phase must be responsible for the high strength in the absence of iron and nickel.

With these two present, the process is reduced to the dispersion of a mixture of aluminides and stannides of these metals in addition to those of manganese.

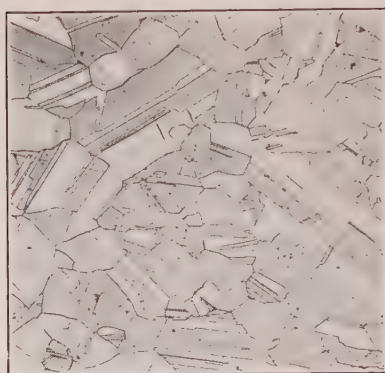


FIG. 7.

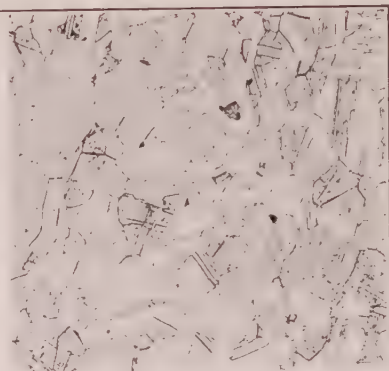


FIG. 8.

FIG. 7.—AN ALLOY, 96 PER CENT. CU, 4 PER CENT. MN, AS ROLLED AND ANNEALED AT 750° C. SHOWS SHARPLY DEFINED ALPHA CRYSTALS, OFTEN TWINNED. $\times 100$.

FIG. 8.—AN ALLOY, 80 PER CENT. CU, 20 PER CENT. MN, ROLLED AND ANNEALED AT 750° C. STRUCTURE IS THE SAME AS IN FIG. 1, CRYSTALS ARE SLIGHTLY BLURRED, HOWEVER, PROBABLY BECAUSE OF THE PRESENCE OF CARBON (0.05 PER CENT. C.). $\times 100$.

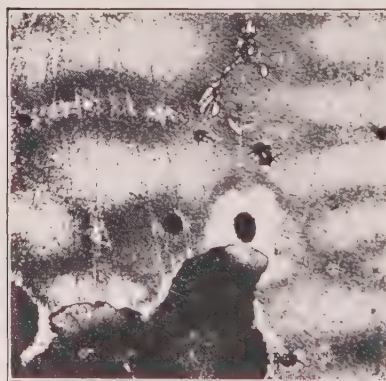


FIG. 9.

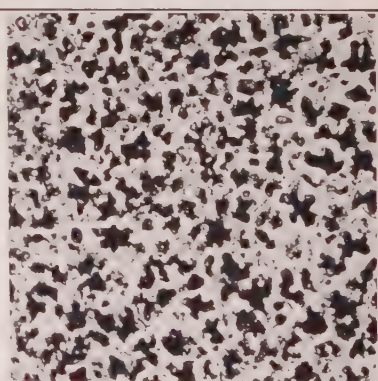


FIG. 10.

FIG. 9.—AN ALLOY, 72 PER CENT. CU, 28 PER CENT. MN, AS CAST AND ANNEALED FOR 2 HR. AT 800° C. CRYSTALS ARE VERY LARGE AND STRONGLY CORED, GRAINLETS OF CARBIDES ARE WITHIN THE DARK CORES. $\times 50$.

FIG. 10.—AN ALLOY, 52 PER CENT. CU, 48 PER CENT. MN, AS CHILL-CAST. CRYSTALS VERY SMALL, EACH CONTAINING A COMPACT, DARK MN-RICH CORE. $\times 100$.

Recently a strong duplex brass specifically intended for extruded bushings has been developed in Germany by adding silicon, in addition to manganese and aluminum, and so embedding hard, plainly visible crystals of manganese silicide within the body of a regular manganese bronze.

Conditions of the same kind probably prevail in the duplex tin and aluminum bronzes, and although no serious investigation has ever been

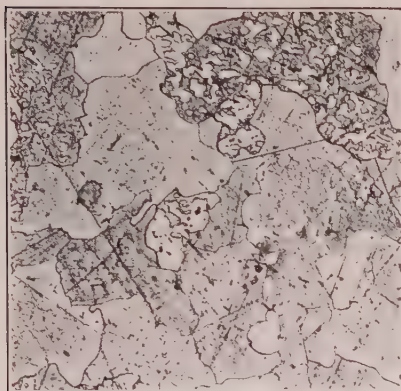


FIG. 11.

FIG. 11.—AN ALLOY, 67 PER CENT. CU, 33 PER CENT. MN, AS CHILL-CAST AND ANNEALED FOR 6 HR. AT 800° C. SOME OF THE CRYSTALS ARE ALREADY FULLY HOMOGENIZED, OTHERS SHOW A NETWORK DUE TO CORING (0.1 PER CENT. C). $\times 100$.

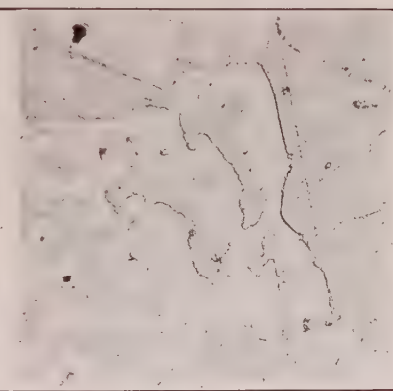


FIG. 12.

FIG. 12.—SAME AS FIG. 11. $\times 500$.

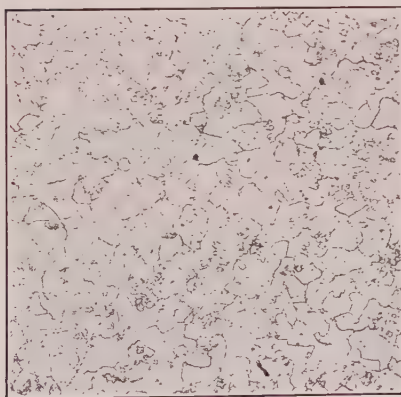


FIG. 13.

FIG. 13.—AN ALLOY, 52 PER CENT. CU, 48 PER CENT. MN, AS CHILL-CAST, ANNEALED FOR 6 HR. AT 800° C. AND QUENCHED. CONTAINS 0.2 PER CENT. C AND 0.5 PER CENT. SI. $\times 100$.

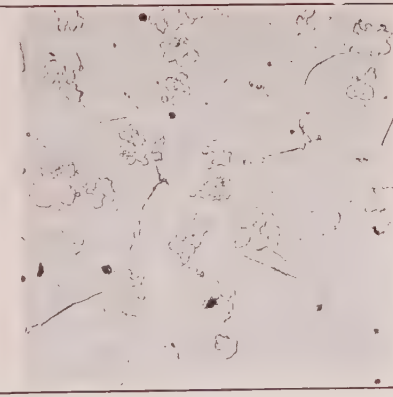


FIG. 14.

FIG. 14.—SAME ALLOY AS IN FIG. 13 AT A HIGHER MAGNIFICATION. A SECOND PHASE IS SEEN IN THE SHAPE OF BRIGHT IRREGULAR GRAINLETS, WHICH MIGHT REPRESENT CARBIDES OR SILICIDES, BUT THEIR CURVED OUTLINES SUGGEST THAT THEY MUST BE OF SOME OTHER MORE DUCTILE SUBSTANCE. $\times 500$.

undertaken of the duplex part of the first series, enough material has been accumulated to show the enormous influence of manganese upon the properties of the duplex aluminum bronzes with about 10 per cent. aluminum.

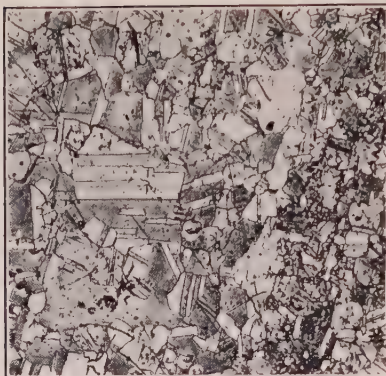


FIG. 15.

FIG. 15.—AN ALLOY, 67 PER CENT. CU, 33 PER CENT. MN, AS ROLLED, ANNEALED AT 800° C. AND QUENCHED. SMALL GRAINLETS ARE SEEN OF A NATURE DIFFERENT FROM GROUNDMASS. $\times 100$.

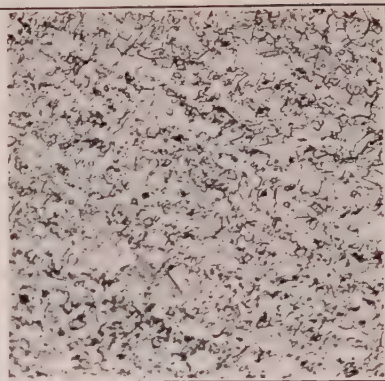


FIG. 16.

FIG. 16.—AN ALLOY, 52 PER CENT. CU, 48 PER CENT. MN, AS ROLLED, ANNEALED AT 800° C. AND QUENCHED. THE GRAINS OF THE GROUNDMASS ARE SMALLER AND THE SECONDARY GRAINLETS ARE MORE NUMEROUS. $\times 100$.

Heusler Alloys

On the one hand the presence of about 15 per cent. manganese causes a considerable decrease in the maximum aluminum content entering the alpha phase. An alloy containing 7 per cent. aluminum plus 15 per cent. manganese possesses a duplex structure and will not be converted to a homogeneous alpha phase by a high-temperature treatment. On the other hand alloys containing slightly larger amounts of aluminum can easily be brought into a homogeneous beta state by raising the temperature to 750° or 800° C.

Alloys containing from 7 to 11 per cent. aluminum and from 20 to 10 per cent. manganese can be hot-rolled with the utmost ease and possess in a general way all mechanical properties, advantages and disadvantages of the duplex aluminum bronzes. They can be heat treated in the same way, by quenching from a high temperature and drawing at a lower one, and rather strong alloys with 100,000 lb. tensile strength, 80,000 lb. yield point and 10 per cent. elongation in 2 in. are so produced. With ternary manganese-aluminum bronzes, just as with the binary duplex aluminum bronzes, quenching brings the material to a state of a high hardness and gives it a martensitic structure. A subsequent drawing somewhere around 600° C. eliminates the internal stresses inherent to the martensitic form with its 270 Brinell and no ductility at all, and a second quenching produces an alloy that is strong and fairly ductile.

When the drawing is done within 600° to 700° C. and is followed by quenching, certain ternary copper-manganese-aluminum alloys acquire a considerable magnetic permeability besides good mechanical proper-

ties. Alloys so heat treated are called Heusler bronzes. (Figs. 17 and 18.) Undoubtedly Heusler initially studied the magnetic properties exclusively, and these, though theoretically interesting, were of no practical use. Heusler's further investigations resulted in the development of

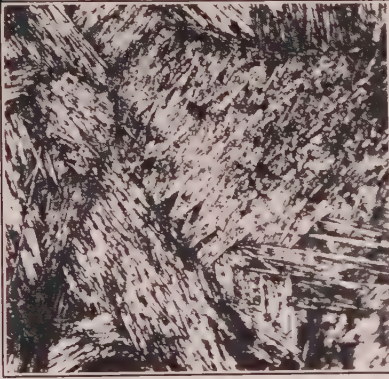


FIG. 17.

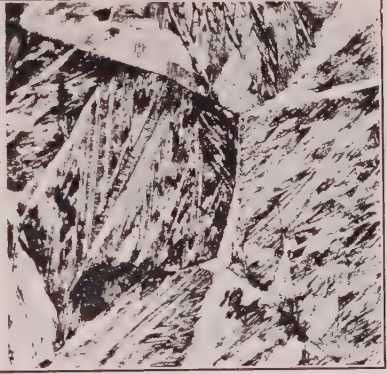


FIG. 18.

FIG. 17.—A HEUSLER BRONZE (15 PER CENT. MN, 10 PER CENT. AL) AS HOT-ROLLED AND QUENCHED FROM 800° C. THE GRAINS ARE CU-MN-AL BETA BRONZE IN THE ACICULAR STATE OF THE EUTECTOIDAL TRANSFORMATION. THIS IS IN THE MAGNETIC STATE. $\times 100$.

FIG. 18.—SAME AS FIG. 17, ADDITIONALLY TREATED AT 620° C. AND QUENCHED. THIS IS THE MAGNETIC STATE. $\times 100$.

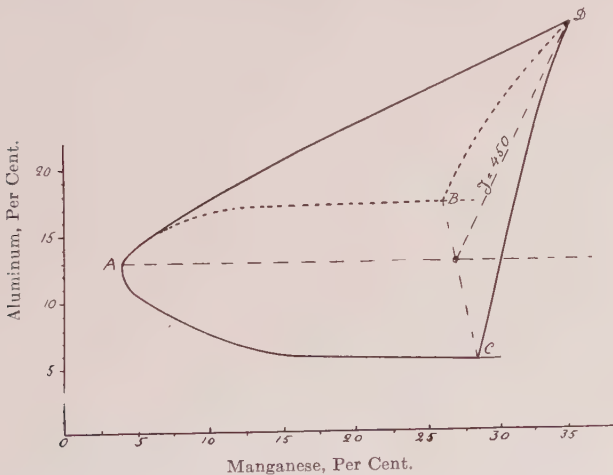


FIG. 19.—COMPOSITION RANGE AND MAGNETIC SUSCEPTIBILITY OF HEUSLER ALLOYS (MANGANESE-ALUMINUM BRONZES).

ternary alloys combining the magnetic properties with a superior strength. The magnetic properties of Heusler's alloys are believed to be due to the presence of the compound Mn_3Al , magnetic in itself and imparting its inherent magnetism almost completely to the beta phase of the aluminum

bronze. Fig. 19 reproduces the constitutional region and magnetic properties of the Heusler alloys. With the present growth of the electric industries, demands will undoubtedly arise, which the magnetic peculiarities of Heusler alloys may accurately fill.

Manganese-aluminum Alloys

In contrast to copper-manganese alloys, with their exceedingly wide range of valuable and useful compositions, the range of useful aluminum-manganese alloys is rather narrow. It is very difficult to dissolve manganese in aluminum unless the latter is heated about 900° to 1100° C. The usual method of making manganese-aluminum alloys on an industrial scale consists in preparing an intermediate alloy with 10 to 15 per cent. manganese by keeping manganese submerged in molten aluminum at a temperature about 1100° C. for a protracted time. Enough intermediate alloy is introduced into molten aluminum in amounts to yield a manganese content of 0.5 to 3.0 per cent. The latter figure is undoubtedly the maximum which can be alloyed with aluminum without badly affecting its ductility. Industrially, the limit of manganese content is set at 2 per cent. and an alloy of this kind plus about 3 per cent. copper is used for castings by the U. S. Navy. Similar amounts of manganese (about 1.2 to 1.5 per cent.) are used in the manufacture of commercial hard aluminum, particularly, for the manufacture of cooking utensils. For high-grade ingot aluminum, containing below 0.5 per cent. iron, the amount of manganese added is about 1.5 per cent., whereas for second-grade ingots (with 0.8 per cent. iron, for instance), it is better to limit the manganese content to 1 per cent.

The third application of manganese in amounts not exceeding 0.8 per cent. is in duralumin type alloys, particularly in the generally used straight duralumin (3 to 5 per cent. copper, 0.5 per cent. magnesium, 0.2 to 0.25 per cent. silicon (as present in the ingot aluminum), and 0.5 to 0.8 per cent. manganese). This addition of manganese is a regular feature of the alloy "17S" (regular duralumin) and of the alloy "25S" which contains no magnesium at all (both made by the Aluminum Co. of America).

The effects of manganese in aluminum alloys are twofold. It always forms a compound Al_3Mn and accordingly a unit of manganese (by weight) results in the formation of 2.5 units of this compound. The latter crystallizes as a rough eutectic between the grains of pure aluminum or of an aluminum-base solid solution (with copper, zinc or magnesium) and considerably decreases the maximum size of the grain developed during the crystallization and the cooling of the cast ingot. In the wrought alloys the aluminum manganese compound acts mainly as a strengthener by interfering with the intergranular slip. During the annealing operation and particularly during the high-temperature treatment (preliminary to quenching of duralumin type alloys), Al_3Mn acts as a grain growth

inhibitor, in this way raising the endurance and proportionality limits of the finished product.

A great number of other elements can be used to replace manganese in its capacity of a grain growth inhibitor and intergranular strengthener. Iron, nickel and chromium are the most available and tractable elements of this kind. In fact, an aluminum-nickel alloy with 2 per cent. nickel forms the *hard aluminum* in Great Britain. There is, however, much to be said in favor of using manganese exclusively.† Manganese is electrochemically the nearest element to aluminum, and its compounds, particularly the Al_3Mn is probably still nearer. Therefore, an *accelerated corrosion*, due to local electric currents, is nearly absent from such hard aluminum as is hardened by manganese. It is very interesting to compare the behavior of alloys containing about 1 per cent. iron and those containing 1 per cent. manganese, respectively on etching. The aluminide of iron will usually be surrounded by corrosion cavities due to local currents. The grainlets of the manganese aluminide and the groundmass of aluminum around them both stay nearly intact, their mutual boundaries remaining sharp and clean.

The paper by Dix and Keith¹² shows that up to 0.6 per cent. manganese the latter is soluble in solid aluminum at 630° C. On cooling the major part seems to precipitate within the grains in the shape of fine, almost submicroscopical particles. The latter seem, however, to be much beyond the critical size and the number of the particles too small to impart to the alloys a considerable hardening by slip inference.

Manganese-silver Alloys

The manganese-silver alloys are a new class, the very existence of which seemed improbable in the light of the scientific investigations of a decade ago. It was believed that manganese could not be alloyed with silver, and that it always formed a separate molten layer. The most recent investigations have proved that up to 20 per cent. (at least) manganese easily alloys with silver, if the alloying is done under a protective slag and the manganese has no chance to oxidize. Up to 9 per cent. manganese goes into solid solution in silver and a manganese-silver alloy of this composition can be worked hot and cold easily; in fact, one could use a silver-manganese solid solution with 92.5 per cent. silver to replace the usual sterling silver were it not for the quick oxidation of the manganese at the surface of the alloy. A slight rubbing suffices to cover the alloy with a brownish looking film. It is possible, however, that some ternary alloys containing both manganese and some other element will prove free from this oxidation (tarnishing).

¹² E. H. Dix, Jr., and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 315.

Mechanically much more important are silver-manganese alloys containing aluminum as the ternary element. They behave as do copper manganese-aluminum alloys with about 15 per cent. manganese and 5 per cent. aluminum. At a high temperature (700° to 850° C.) manganese and aluminum both go into the alpha solid solution. By using a process of heat treatment consisting of quenching from a high temperature (750° to 850° C.) and drawing at a much lower one (200° to 300° C.), alloys of 60,000 lb. ultimate strength, 120 Brinell and 10 per cent. elongation in 2 in. are produced. It seems as if these alloys are much less inclined to tarnish than pure or sterling silver. Unfortunately, the maximum amount of silver at which the hardening effect still takes place is far below the legal limit of 92.5 per cent. for silverware manufacture. It is possible, however, that such alloys might find applications for other industrial or ornamental purposes.

DISCUSSION

Z. JEFFRIES, Cleveland, O.—I would like to add to the other information in the paper that manganese has a very important effect in the magnesium-base alloys which also contain aluminum. Nearly pure magnesium has a certain resistance to general corrosion. If aluminum is added to the magnesium the physical properties are very substantially improved, but corrosion resistance is very substantially impaired. By adding manganese to these binary alloys of magnesium and aluminum, the good physical properties are preserved and the good corrosion resistance of magnesium is also preserved.

E. H. DIX, JR., and W. D. KEITH, New Kensington, Pa. (written discussion).—We desire to confine our discussion of this very valuable paper by Mr. Corson to the section that he has devoted to aluminum-manganese alloys, and particularly to the reference he has made to our recent paper on Equilibrium Relations in Aluminum-manganese Alloys of High Purity.

It was shown in our paper that a chill-cast aluminum-manganese alloy containing as much as 2 per cent. manganese showed comparatively few particles of constituent when examined microscopically, and that a short time annealing at, say, 500° C. caused the appearance of fine, almost submicroscopic particles. Since the solid solubility was found to be probably not over 0.65 per cent., it was evident that the appearance of these particles was not caused by precipitation from solid solution but rather by coalescence of submicroscopic eutectic particles produced by under cooling during chill casting.

The inference in Mr. Corson's statement that "on cooling the major part seems to precipitate within the grains in the shape of fine, almost submicroscopical particles" is not in accord with our conclusion. At the time, we suggested the term "dispersoid" to describe these finely dispersed particles in anticipation that this phenomenon would be confused with the more familiar precipitation from solid solution.

We would like also to express as our opinion that manganese does not always form the compound $MnAl_3$ in aluminum alloys, as Mr. Corson has stated, but that it enters much more complex constituents when other elements are present. For instance, we have never observed the compound $MnAl_3$ in duralumin. These observations were expressed in our paper on Etching Characteristics of Constituents in Commercial Aluminum Alloys, presented before the A. S. T. M. last year.

Alpha Phase Boundary of the Copper-nickel-tin System

BY WM. B. PRICE,* PH. B., C. G. GRANT,† M. S., AND A. J. PHILLIPS,‡ M. S.,
WATERBURY, CONN.

(New York Meeting, February, 1928)

ADMIRALTY nickel is a new corrosion-resisting and heat-resisting white metal alloy composed of 70 per cent. copper, 29 per cent. nickel and 1 per cent. tin. It has been given the trade name "Adnic." In 1924, Wm. B. Price¹ described this alloy and its successful use as a diaphragm metal. The physical properties of Adnic at ordinary and elevated temperatures were given in *Mining & Metallurgy*.² A patent³ was granted on Adnic, April 28, 1925.

Work was first started on this alloy during December, 1921. An investigation of the patent situation in this country and abroad, and also a search of the literature, did not reveal any work on the ternary diagram, copper-nickel-tin; and the only wrought copper-nickel-tin alloy found was that known as "Newloy," composed of copper, 64 per cent.; nickel, 35 per cent.; tin, 1 per cent. This was being manufactured and sold by Wm. Gallimore & Sons, Ltd., Sheffield, England, for unplated spoon and fork stock, and first came to our attention in January, 1922.

The preliminary work in connection with the development of Adnic was started by casting four binary copper-nickel alloys of the compositions shown in Table 1. Various amounts of tin were added to each of these mixtures, to produce the series of ternary copper-nickel-tin alloys also given in Table 1. A 200-gm. sample of each of these was cast by melting in a clay graphite crucible and allowing the melt to slowly cool with the furnace.

A longitudinal section from each of these castings was polished and etched for examination. The castings were not homogeneous solid solutions, but showed the usual cored structure associated with cast alloys. However, from an examination of these sections we roughly determined

* Chief Chemist and Metallurgist, Scovill Mfg. Co.

† Metallurgist, Scovill Mfg. Co. (died Jan. 27, 1928).

‡ Metallurgist, Scovill Mfg. Co.

¹ Wm. B. Price: General discussion, symposium on corrosion-resistant alloys. *Proc. A. S. T. M.* (1924) **24**, Pt. 2, 422.

² Wm. B. Price: Physical Properties of Adnic. *Min. & Met.* (November, 1927) **8**, 474.

³ Wm. B. Price: U. S. Patent No. 619773.

TABLE 1.—*Alloys Used in Developing Adnic*

COMPOSITION OF BINARY ALLOYS			
No.	Copper, Per Cent.	Nickel, Per Cent.	
A	90	10	
B	80	20	
C	70	30	
D	60	40	

COMPOSITION OF TERNARY ALLOYS			
No.	Copper, Per Cent.	Nickel, Per Cent.	Tin, Per Cent.
A-1	84.5	9.5	6.0
A-2	83.7	9.3	7.0
A-3	82.8	9.2	8.0
A-4	81.9	9.1	9.0
B-1	76.0	19.0	5.0
B-2	75.2	18.8	6.0
B-3	74.4	18.6	7.0
B-4	73.6	18.4	8.0
C-1	66.5	28.5	5.0
C-2	65.8	28.2	6.0
C-3	65.1	27.9	7.0
C-4	64.4	27.6	8.0
C-5	63.7	27.3	9.0
C-6	63.0	27.0	10.0
C-7	59.5	25.5	15.0
C-8	56.0	24.0	20.0
C-9	52.5	22.5	25.0
C-10	49.0	21.0	30.0
D-1	57.6	38.4	4.0
D-2	57.0	38.0	5.0
D-3	56.4	37.6	6.0
D-4	55.8	37.2	7.0

the dividing line between the alpha and alpha plus beta solid solutions of copper, nickel and tin within the limits of the compositions investigated. The location of the alpha phase boundary is shown in Fig. 1.

Some idea of the appearance of alloys A-4, B-4, C-3, C-7, C-8, C-9, C-10 and D-3, can be obtained from Figs. 2 to 9. These photomicrographs of slowly cooled melts all disclose the presence of a secondary constituent. Those of series C, representing alloys with a 70 to 30 copper nickel ratio, show the structural modifications caused by varying the tin content from 7 to 30 per cent.

TABLE 2.—*Alloys of Binary Systems Containing Varying Amounts of Tin*

No.	Base		Cu, Per Cent.	Ni, Per Cent.	Sn, Per Cent.	Constituents
	Cu.	Ni.				
159M	100	0	88.1	0	11.9	Alpha
112M	100	0	87.5	0	12.5	Alpha
51M	100	0	87.0	0	13.0	Alpha
113M	100	0	86.5	0	13.5	Alpha plus trace of beta
69M	100	0	85.0	0	15.0	Alpha plus beta
70M	100	0	82.0	0	18.0	Alpha plus beta
60M	90	10	84.2	9.3	6.5	Alpha
43M	90	10	83.3	9.3	7.4	Alpha
52M	90	10	82.5	9.2	8.3	Alpha
71M	90	10	81.9	9.1	9.0	Alpha
160M	90	10	81.1	9.0	9.9	Alpha
115M	90	10	81.0	9.0	10.0	Alpha plus trace of beta
133M	90	10	80.1	8.9	11.0	Alpha plus beta
61M	80	20	74.8	18.7	6.5	Alpha
134M	80	20	74.4	18.6	7.0	Alpha
161M	80	20	74.2	18.5	7.3	Alpha
116M	80	20	73.6	18.4	8.0	Alpha plus trace of beta
78M	80	20	72.8	18.2	9.0	Alpha plus beta
74M	80	20	72.0	18.0	10.0	Alpha plus beta
54M	70	30	65.4	28.1	6.5	Alpha
75M	70	30	64.4	27.6	8.0	Alpha
162M	70	30	64.2	27.5	8.3	Alpha plus trace of beta
119M	70	30	63.7	27.3	9.0	Alpha plus beta
55M	60	40	56.6	37.7	5.7	Alpha
62M	60	40	56.1	37.4	6.5	Alpha
85M	60	40	55.5	37.0	7.5	Alpha
103M	60	40	55.2	36.8	8.0	Alpha
104M	60	40	54.6	36.4	9.0	Alpha
163M	60	40	54.5	36.4	9.1	Alpha
121M	60	40	54.0	36.0	10.0	Alpha plus trace of beta
86M	50	50	46.5	46.5	7.0	Alpha
92M	50	50	46.2	46.2	7.6	Alpha
94M	50	50	45.8	45.8	8.4	Alpha
105M	50	50	45.0	45.0	10.0	Alpha
122M	50	50	44.5	44.5	11.0	Alpha
123M	50	50	44.0	44.0	12.0	Alpha plus beta
109M	50	50	43.5	43.5	13.0	Alpha plus beta
93M	40	60	37.2	55.8	7.0	Alpha
106M	40	60	35.2	52.8	12.0	Alpha
124M	40	60	34.8	52.2	13.0	Alpha plus trace of beta
110M	40	60	34.4	51.6	14.0	Alpha plus beta
95M	30	70	27.3	63.7	9.0	Alpha
96M	30	70	26.4	61.6	12.0	Alpha
107M	30	70	26.1	60.9	13.0	Alpha
111M	30	70	25.8	60.2	14.0	Alpha plus trace of beta
102M	30	70	25.5	59.5	15.0	Alpha plus beta
137M	20	80	17.2	68.8	14.0	Alpha
141M	20	80	17.0	68.0	15.0	Alpha plus trace of beta
142M	20	80	16.6	66.4	17.0	Alpha plus beta
143M	20	80	16.2	64.8	19.0	Alpha plus beta
135M	10	90	8.5	76.5	15.0	Alpha
144M	10	90	8.2	73.8	18.0	Alpha plus beta
145M	10	90	8.0	72.0	20.0	Alpha plus beta
146M	10	90	7.8	70.2	22.0	Alpha plus beta
151M	0	100	0	85.0	15.0	Alpha plus trace of beta
147M	0	100	0	80.0	20.0	Alpha plus beta
148M	0	100	0	78.0	22.0	Alpha plus beta
149M	0	100	0	76.0	24.0	Alpha plus beta
150M	0	100	0	74.0	26.0	Alpha plus beta

In view of the many interesting solid-solution alloys disclosed by this preliminary investigation, it was decided to carry on a research to more definitely fix the alpha phase boundary of the copper-nickel-tin system.

Since copper and nickel are completely soluble in each other in all proportions, even when solid, it was decided to subdivide the ternary diagram into eleven binary systems, of which one component was always pure tin and the other varied from pure copper to pure nickel in steps of

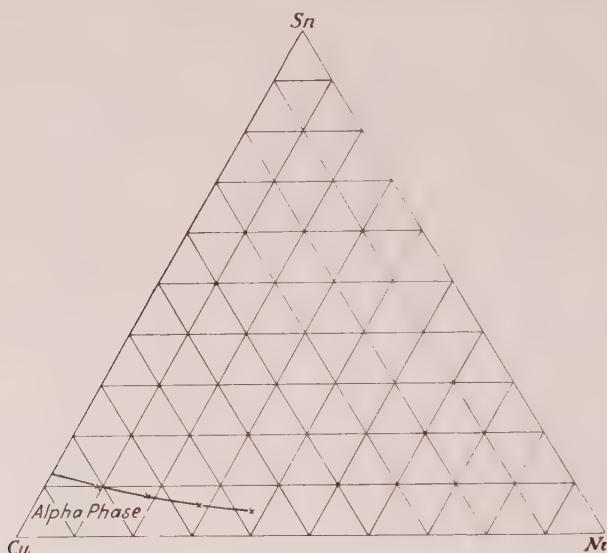
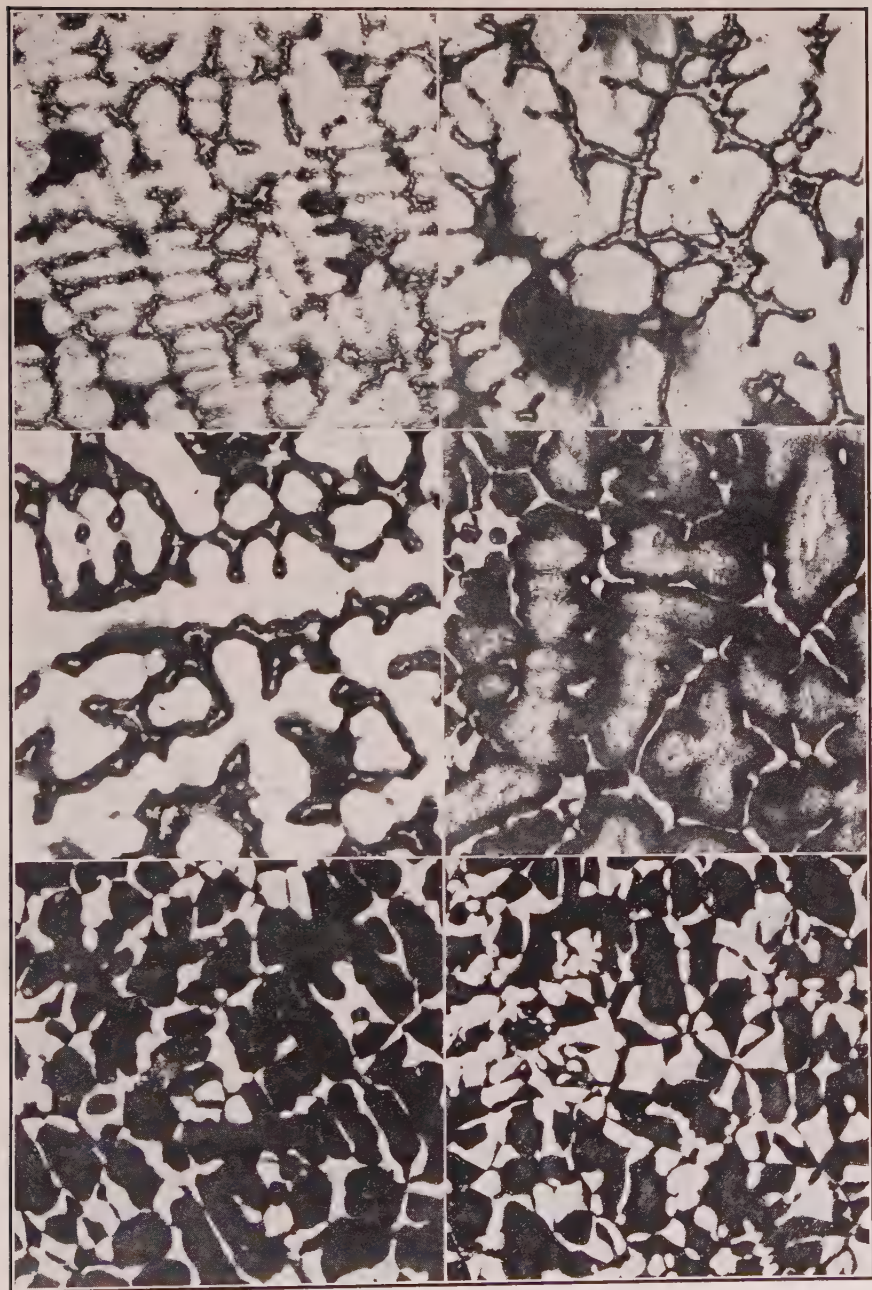


FIG. 1.—APPROXIMATE LOCATION OF ALPHA PHASE BOUNDARY, Cu-Ni-Sn SYSTEM, AS PLOTTED FROM THE MICRO-EXAMINATION OF SLOWLY COOLED CASTINGS.

10 per cent. Alloys of each of these binary systems containing varying percentages of tin (as listed in Table 2) were prepared by melting down 100-gm. charges under charcoal in a clay graphite crucible, and then chill casting in a relatively heavy iron mold. The ingots so obtained were cut in half, providing one section for micrographic examination as cast, and the other for homogenizing treatment. This consisted of annealing at 800° C. for at least 100 hr. and then quenching actively in water.

- FIG. 2.—ALLOY No. A-4. COPPER 81.9 PER CENT.; NICKEL 9.1 PER CENT.; TIN 9.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.
 FIG. 3.—ALLOY No. B-4. COPPER 73.6 PER CENT.; NICKEL 18.4 PER CENT.; TIN 8.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.
 FIG. 4.—ALLOY No. C-3. COPPER 65.1 PER CENT.; NICKEL 27.9 PER CENT.; TIN 7.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.
 FIG. 5.—ALLOY No. C-7. COPPER 59.5 PER CENT.; NICKEL 25.5 PER CENT.; TIN 15.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.
 FIG. 6.—ALLOY No. C-8. COPPER 56.0 PER CENT.; NICKEL 24.0 PER CENT.; TIN 20.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.
 FIG. 7.—ALLOY No. C-9. COPPER 52.5 PER CENT.; NICKEL 22.5 PER CENT.; TIN 25.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.



FIGS. 2 TO 7.

Microstructures observed in all specimens are noted in Column 7, Table 2, and the phase boundary thus outlined is shown in Fig. 10.

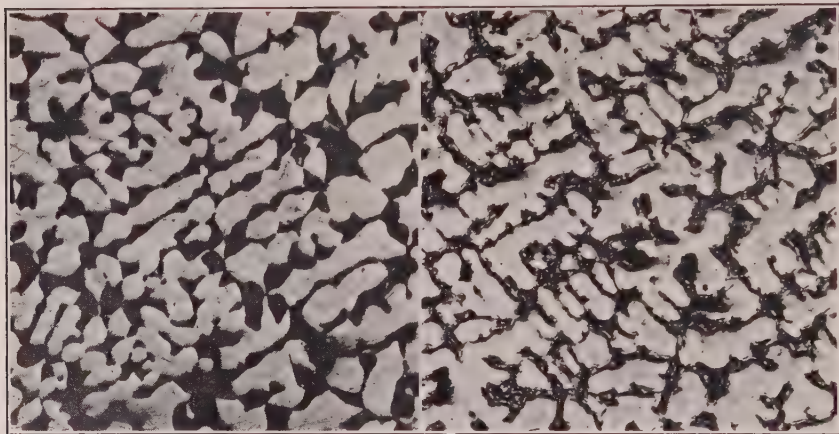


FIG. 8.—ALLOY No. C-10. COPPER 49.0 PER CENT.; NICKEL 21.0 PER CENT.; TIN 30.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.

FIG. 9.—ALLOY No. D-3. COPPER 56.4 PER CENT.; NICKEL 37.6 PER CENT.; TIN 6.0 PER CENT. ETCHED WITH $\text{FeCl}_3 + \text{HCl}$. $\times 75$.

Alloy 134M, containing 7 per cent. tin added to an 80-20 copper-nickel base, is illustrated in Fig. 11. Only one metallic phase is present,

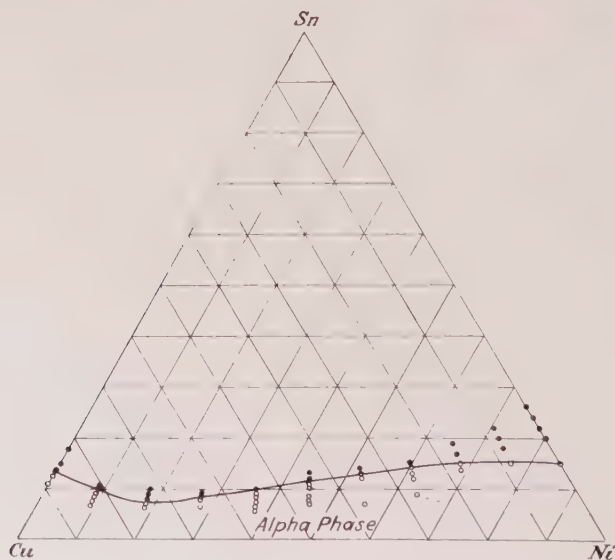


FIG. 10.—800° ISOTHERM OF ALPHA PHASE BOUNDARY, CU-NI-SN SYSTEM.

the black spots visible being very small cavities, probably formed by the volume change that occurred when the metastable secondary constituent

was absorbed by the denser alpha phase. Fig. 12 shows the same base alloy with 8 per cent. tin. The presence of beta in the grain boundaries is quite apparent. Like Fig. 11, Fig. 13 shows a single-phase alloy made from 50-50 copper-nickel base plus 11 per cent. tin. Fig. 14, containing 12 per cent. tin, clearly shows beta in the grain boundaries.

Fig. 15 represents an alloy made from a 20-80 copper-nickel base to which was added 14 per cent. tin, without the separation of a second phase. A similar base alloy but with 17 per cent. tin is shown in Fig. 16. The beta in this case is visible not only in the grain boundaries but also within the grains. This condition is brought out very distinctly by permitting the alpha constituent to stain in a strong ferric chloride solution, as illustrated in Fig. 17.

The use of charcoal as a cover for nickel alloys may be considered doubtful practice but a few experiments with alloys at the nickel end of the series, melted under a borax glass cover, demonstrated that the alpha phase boundary was not perceptibly influenced by small amounts of carbon. Analyses of the alloys were not made because there was no loss of any constituent in alloying, either by volatilization or by slagging. The weights of the cast ingot and of the original charge were almost always identical.

As only a limited amount of time was available for this work, the single annealing temperature of 800° C. was decided upon, because it was the maximum temperature to which alloys at the copper end of the series could be subjected without danger of melting.

Since neither the copper-tin diagram as revised by Stockdale⁴ nor the nickel-tin diagram as determined by Voss⁵ indicated decreasing tin solubility at lower temperatures, it was thought that the rate of cooling after annealing was immaterial. However, it was early found that an alloy of 90-10 copper-nickel base, containing 8.3 per cent. tin, showed no beta when quenched from 800° C. but when slowly cooled was completely "peppered" with a second constituent.

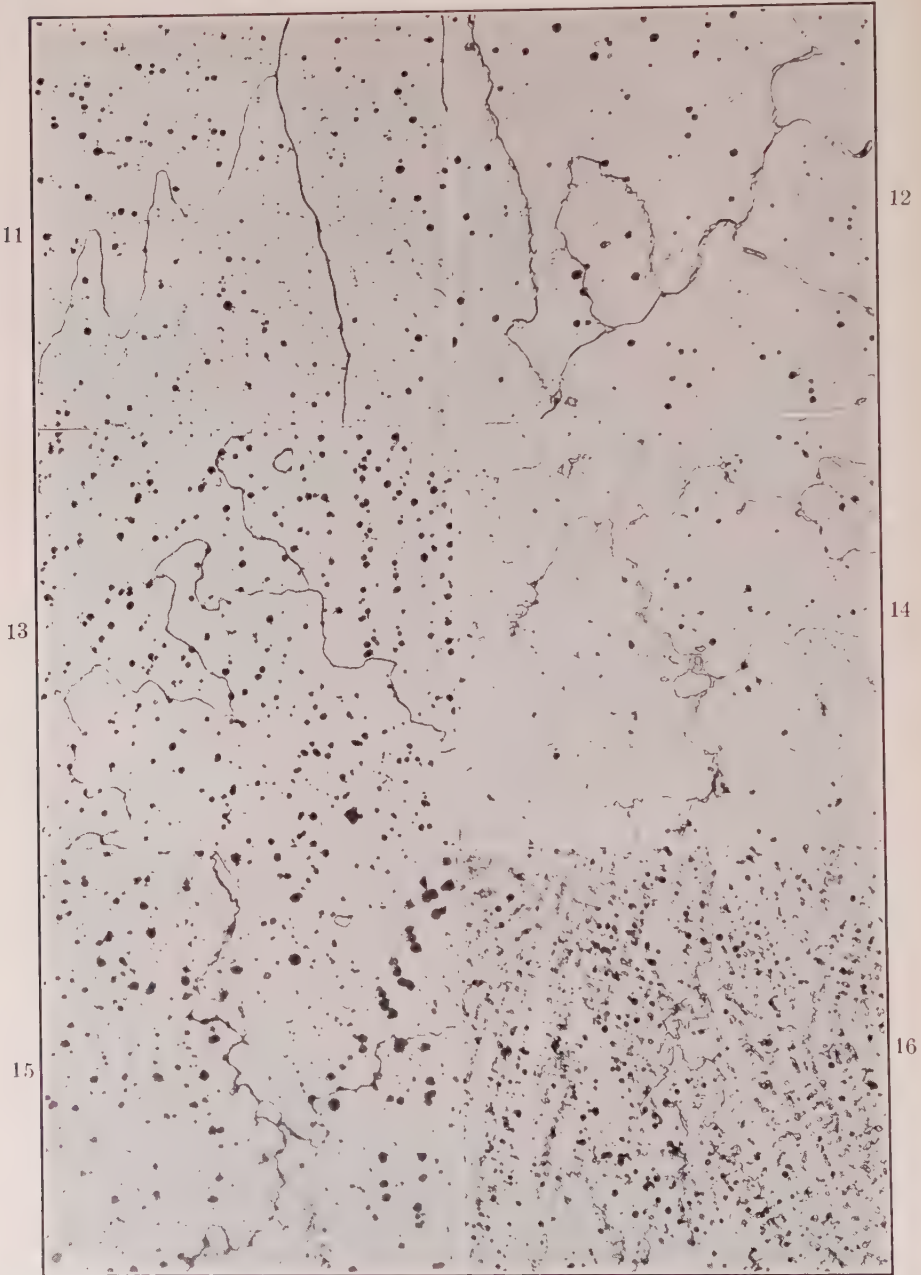
These results, coupled with the knowledge that Dr. J. L. Haughton had suggested, in his discussion of Stockdale's paper,⁶ that the copper-tin diagram should show decreasing solubility of tin at lower temperatures, stimulated us to attempt to prove this. Therefore, several experiments were performed with a copper alloy containing 15 per cent. tin, and demonstrated beyond doubt that a second constituent separated from the alpha phase, when annealed for a long period of time at 250° C. In view of the fact that M. Hansen⁷ has recently established the same results

⁴ D. Stockdale: Alpha-phase Boundary in the Copper-tin System. *Jnl. Inst. Met.* (1925) **34**, 111.

⁵ G. Voss: Die Legierungen Nickel zinn, etc. *Zeitschr. anorg. Chem.* (1908) **57**, 38.

⁶ *Jnl. Inst. Met.* (1925) **34**, 121.

⁷ O. Bauer and M. Hansen: Der Aufbau der Kupfer-Zinklegierungen. *Zeitschr. für Metall.* (1927) **19**, 423.



FIGS. 11 TO 16.

with a more thorough series of tests, a description of our experiments is not included here.

Additions of small amounts of nickel caused the slope of the tin-solubility line to decrease; consequently a very active quench was necessary in the case of a 90-10 base alloy to prevent a precipitation from the supersaturated solid solution. With larger additions of nickel, the metal became more and more sluggish, so that an active quench was not imperative in the case of 70-30 base alloys.

This condition of affairs suggested to us* that these alloys might be hardened in a way similar to that used for duralumin; *i. e.*, by quenching at an elevated temperature and drawing at a lower temperature. A series of experiments was performed to demonstrate this property. A charge consisting of 64.4 per cent. copper, 27.6 per cent. nickel and 8 per cent. tin, and weighing 2000 gm., was melted and chill cast, yielding a rod 1 in. in diameter and 18 in. long. From it, six sections, $\frac{3}{8}$ in. thick, were cut and subsequently annealed for 100 hr. at 800° C. Four of the specimens were quenched, one was air-cooled and one furnace-cooled. Of the specimens quenched, one was reannealed or "drawn" for one hour at 400° C., a second at 500° C. and a third at 600° C. Table 3 gives Brinell hardness numbers for the various treated specimens. From a study of the microstructures of the specimens, we are convinced that a Brinell value even higher than 321 can be produced by an intermediate anneal between 400° and 500° C.

Fig. 18 illustrates the appearance of the original casting. We are not attempting to describe the constituents, for fear of becoming involved in a controversy as to the possible beta-gamma-delta transformations. The completely homogenized specimen is not illustrated, as its appearance is like that shown in Figs. 11, 13 or 15. The same is true of the air-cooled specimen. The structure of the furnace-cooled specimen is most interesting, and is illustrated by Fig. 19, in which it should be noticed that there are three different structures visible. The black areas

FIG. 11.—ALLOY 134M. COPPER 74.4 PER CENT.; NICKEL 18.6 per cent.; TIN 7 PER CENT.; ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.

FIG. 12.—ALLOY 116M. COPPER 73.6 PER CENT.; NICKEL 18.4 PER CENT.; TIN 8 PER CENT. ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.

FIG. 13.—ALLOY 122M. COPPER 44.5 PER CENT.; NICKEL 44.5 PER CENT.; TIN 11 PER CENT. ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.

FIG. 14.—ALLOY 123M. COPPER 44.0 PER CENT.; NICKEL 44.0 PER CENT.; TIN 12 PER CENT. ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.

FIG. 15.—ALLOY 137M. COPPER 17.2 PER CENT.; NICKEL 68.8 PER CENT.; TIN 14 PER CENT. ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.

FIG. 16.—ALLOY 142M. COPPER 16.6 PER CENT.; NICKEL 66.4 PER CENT.; TIN 17 PER CENT. ANNEALED 100 HR. AT 800° C. AND QUENCHED. ETCHED WITH CrO_3 + HCL . $\times 100$.



FIGS. 17 TO 22.

appear to be caused by a heavy precipitation of secondary constituent, as may be ascertained from Fig. 20 and Fig. 21. The light gray areas show some precipitation, as is illustrated in Fig. 22. Upon casual examination, the white areas appeared to be relatively free from precipitate, but under critical conditions of illumination, a second phase could occasionally be detected.

TABLE 3.—*Hardness Produced in Alloys*

Alloy No.	Condition	Brinell Hardness No.
173M	As cast.....	114
173M1	Homogenized and quenched.....	100
173M2	Homogenized and furnace-cooled.....	196
173M3	Homogenized and air-cooled.....	114
173M4	Homogenized and drawn at 400° C.....	228
173M5	Homogenized and drawn at 500° C.....	321
173M6	Homogenized and drawn at 600° C.....	179

The specimen drawn at 400° C. is not illustrated because its structure was not modified perceptibly by the anneal. There was a hint of broad-

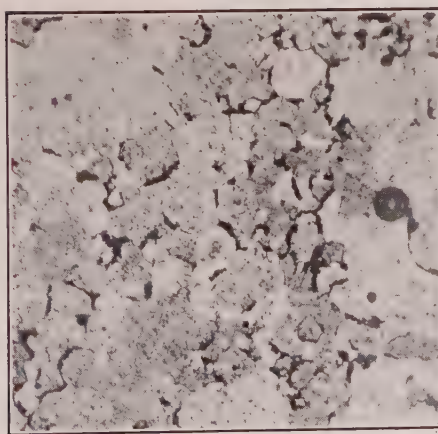


FIG. 23.—ALLOY SHOWN IN FIG. 18. ANNEALED 100 HR. AT 800° C. AND QUENCHED. DRAWN 1 HR. AT 500° C. ETCHED WITH $\text{CrO}_3 + \text{HCL}$. $\times 50$.

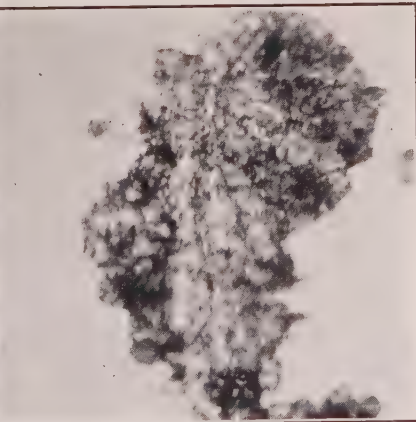


FIG. 24.—SAME AS FIG. 23 AT $\times 1000$.

ening of the grain boundaries but it was too indefinite to be illustrated. Fig. 23 illustrates the appearance of the sample as "drawn" at 500° C.

FIG. 17.—SAME AS FIG. 16 BUT ETCHED WITH FeCl_3 . $\times 100$.

FIG. 18.—ALLOY 173M. COPPER 64.4 PER CENT.; NICKEL 27.6 PER CENT.; TIN 8 PER CENT. CHILL CAST. ETCHED WITH $\text{CrO}_3 + \text{HCL}$. $\times 100$.

FIG. 19.—ALLOY SHOWN IN FIG. 18. ANNEALED 100 HR. AT 800° C. AND FURNACE-COOLED. ETCHED WITH $\text{CrO}_3 + \text{HCL}$. $\times 50$.

FIG. 20.—SAME AS FIG. 19 BUT $\times 750$.

FIG. 21.—A DARK AREA IN FIG. 19 AT $\times 1000$.

FIG. 22.—A LIGHT GRAY AREA IN FIG. 19 AT $\times 2000$.

Unsuccessful attempts were made to resolve the black constituent in the grain boundaries, as illustrated in Fig. 24. The annealing treatment at 600° C. gave a specimen that upon etching behaved very much like sorbitic steel. It seemed to smudge *all over* and the grain boundaries were not developed. Only at high powers could a rather indefinite structure be discerned, as illustrated by Fig. 25.

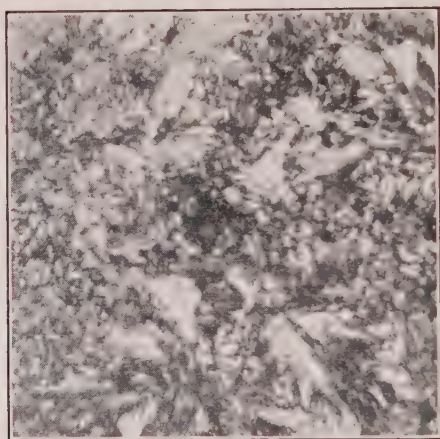


FIG. 25.—ALLOY SHOWN IN FIG. 18. ANNEALED 100 HR. AT 800° C. AND QUENCHED DRAWN 1 HR. AT 600° C. ETCHED WITH $\text{CrO}_3 + \text{HCl}$. $\times 1000$.

SUMMARY

1. The 800° C. isotherm of the alpha phase boundary of the copper-nickel-tin system was determined as shown in Fig. 10.
2. Hansen's determination of the alpha phase boundary at low temperatures for the copper-tin system has been confirmed.
3. A wide range of hardenable copper-nickel-tin alloys has been discovered.

When starting this work, it was our intention merely to determine the single isotherm given in Fig. 10, but the very interesting hardenable alloys discovered have encouraged us to do further work and we now contemplate the locating of the phase boundary over its entire range. Later, we hope to publish the results.

DISCUSSION

E. M. WISE, Bayonne, N. J.—I have been interested in the copper-nickel-tin alloys for some years. These alloys were first studied at the Wadsworth Watch Case Co. in an investigation of base-metal alloys suitable for parts of gold-filled watch cases.

A number of copper-nickel-tin alloys were made up, some of them containing also a small amount of silicon or chromium, which increases the strength at the expense of ductility. The physical properties of a few of these alloys are shown in Table 4.

The age-hardening characteristics of these alloys, as well as the similar behavior of the copper-nickel-phosphorus, copper-manganese-silicon and copper-nickel-silicon alloys, were discovered.

The solubility relations existing at the copper end of the copper-nickel-tin system are shown in Fig. 26. The pronounced change in solubility between 800° and 300° C.

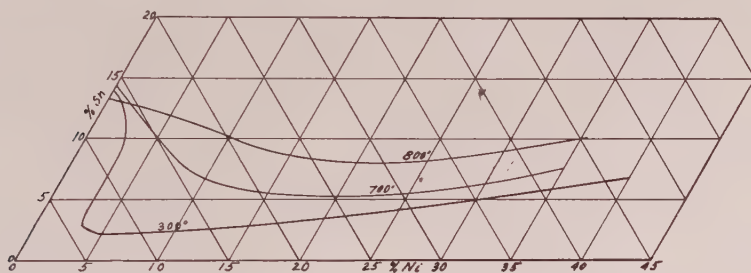


FIG. 26.—EQUILIBRIUM DIAGRAM OF COPPER-NICKEL-TIN ALLOYS.

for alloys containing from about 4 per cent. to perhaps 55 per cent. nickel indicates desirable age-hardening characteristics. The 800° solubility agrees with the determinations of Price and Phillips.

Fig. 27 shows the hardness changes exhibited by two copper-nickel-tin alloys, which had been cold rolled and treated as indicated on the diagram. The specimens were heated to the temperature indicated and were held for 1 hr. One set of samples had been cold rolled 50 per cent. before treating, while the other set had been annealed at 750° for 1 hr. followed by quenching.

TABLE 4.—*Tensile Properties of Some Copper-nickel-tin Alloys*

Composition							Tensile Properties			
Cu	Ni	Sn	Si	Cr	Mn	Zn	Heat Treatment ½ Hr., Degrees Cent.	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Per Cent. Elong. in 2 In.
87.5	5.0	7.0	0.5				650	56,000	80,250	32.0
							750	44,000	71,500	39.6
86.0	7.5	5.0		0.5			700	36,900	66,200	37.5
							750	29,700	63,500	38.0
86.5	8.0	5.0	0.5				700	48,000	74,000	33.5
							750	45,800	73,300	36.5
65.0	27.5	6.0		0.5			700	58,900	92,500	31.0
							750	54,200	90,000	35.0
66.0	27.5	6.0		0.2	0.3		750	43,100	82,500	38.5
							700	51,600	86,200	36.5
63.7	28.0	6.0			0.3	2.0	700	42,500	86,300	37.0
							750	35,100	79,300	

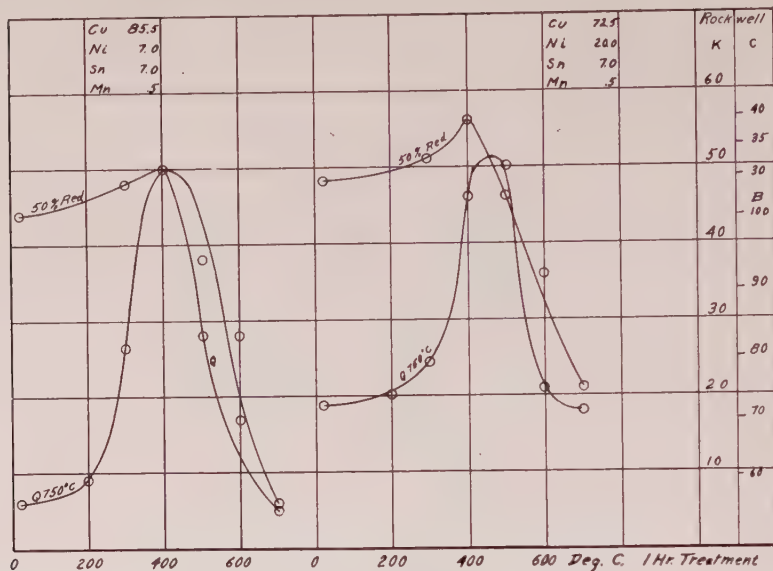


FIG. 27.—ANNEALING AND AGING CHARACTERISTICS OF ROLLED COPPER-NICKEL-TIN ALLOYS.

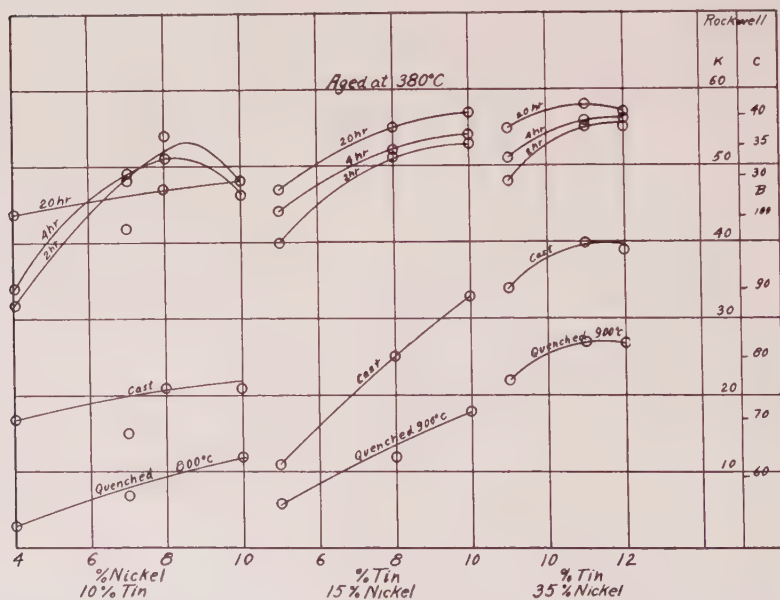


FIG. 28.—VARIATION OF HARDNESS WITH COMPOSITION AND HEAT TREATMENT OF CHILL-CAST COPPER-NICKEL-TIN ALLOYS.

An alloy containing 85 per cent. copper, 7.4 nickel and 7.6 tin showed a tensile strength of 61,000 lb. per sq. in. as quenched. After aging at 300° C. for 3 hr., the tensile strength increased to 105,500 lb. per sq. in. Alloys containing approximately 8 per cent. of tin and about 7 per cent. of nickel machine very well, particularly after slow cooling, which develops a pearlitic structure. The slowly cooled alloy is rather brittle and machines to a beautiful finish, even in the absence of lead. Alloys containing about 7 per cent. Sn and 7 per cent. Ni cold work very well and can be swaged and drawn into wire without difficulty.

Fig. 28 indicates the hardness values observed in a series of small chill castings, as cast, after annealing and quenching, and after aging. The hardness values denoted by *K* were obtained by using 100-kg. load and the diamond penetrator on the Rockwell machine. Approximate values in terms of the Rockwell B and C scale are also given.

The hardest alloy that I have produced contained 40 per cent. of nickel and 15 per cent. of tin, which after aging reached 49 Rockwell C, which is quite hard for a non-ferrous alloy.

I present no photomicrographs because, as Mr. Phillips said, the structures are difficult to resolve and are not materially different from the precipitate structures met with in other alloys.

I believe that there is a distinct field of usefulness for these alloys as casting alloys. Castings of this material should be annealed and rapidly cooled and then aged for a suitable time. Some increase in hardness may be obtained by aging castings without the prior anneal, but preferably annealing should precede the aging. Certain treatments can be utilized to develop structures that make the material particularly desirable for use when subjected to high bearing pressures.

E. H. DIX, JR., New Kensington, Pa.—The figures in the paper show a number of small black pits. It is suggested by the authors that these are due to a volume change caused by one of the constituents being dissolved in the matrix. I wonder if that is the true explanation. We have done considerable work involving the solution of one constituent in another. We feel that this is accomplished by interchange of atoms since we have not found any evidence of such porosity. However, in some of the heat-treatable aluminum alloys, if the heat-treating temperature is too high, we find similar black pits which we believe to be due to the melting of a low melting complex. I wonder if in the system under discussion there may be possibility of some ternary or other low melting eutectics which have not been discovered, and perhaps the annealing temperature of 800° C. has been sufficient to cause melting of those constituents.

A. J. PHILLIPS.—Our accounting for those black holes is merely an assumption on our part and there certainly is almost any possibility in the copper-tin system of low melting eutectics or compounds existing.

Distribution of Tensile Strength in Hard Drawn Copper Wire

BY FRANK W. HARRIS,* BALTIMORE, MD.

(New York Meeting, February, 1928)

THE strength of hard drawn copper wire is a question of considerable importance to both manufacturer and consumer. Unlike steel and alloy wires, in which strength is governed by both chemical and physical considerations, the high conductivity required for copper wire in the electrical industry generally precludes the possibility of obtaining tensile strength through the use of alloys.

Consequently, this strength is largely a matter of the physical structure, and all factors known to affect this structure, such as rolling temperature, die contours, lubricants, drawing speeds, etc., are matters of prime importance.

The experiments described here have been carried out during the past year at the Baltimore plant of the American Smelting & Refining Co., in connection with a general investigation of some of the questions mentioned above, with the object of studying the physical structure of hard drawn copper wire and the influence of certain factors on that structure. The work has been of an exploratory nature, rather than comprehensive, but it was thought that the results might prove of sufficient general interest to warrant their publication.

The bulk of the hard drawn copper wire used in places where strength is an important factor is manufactured to strict specification, based usually in the United States on that of the American Society for Testing Materials (B-1-23). This specification calls for almost as high a value of tensile strength, consistent with elongation, as it is possible practically to obtain, and only physically perfect material can be relied on to meet such a specification. Obvious defects, such as laminations produced through fins in the original rods or brittleness due to overdrawing, are usually recognized and need only passing reference.

Laminations can be detected by twisting and untwisting the wire several times; they will show up on the surface in the form of fins. Fig. 1 shows a very bad example of this defect. The wire may be perfectly smooth before twisting but when such laminations are present they will readily show up under this treatment. This trouble is caused by similar defects in the original rod produced by overfills in rolling. Fig. 2 shows the cross-section of the rod from which the wire in Fig. 1 was drawn.

* Physicist, American Smelting & Refining Co.

Structural brittleness is another common cause of low strength. It may be generally recognized by a pronounced "cup and cone" fracture when the wire is bent through a comparatively small angle. This type of brittleness is generally produced during drawing, although the original rods are often wrongly blamed for the trouble. It is found in both ferrous and non-ferrous wire and may be produced in several ways, each tending

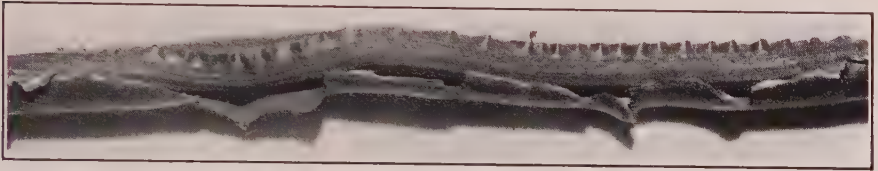


FIG. 1.—LAMINATIONS IN DEFECTIVE WIRE REVEALED BY TWISTING AND UNTWISTING.
 $\times 6$.
 (Reduced to 85 per cent. original scale, original magnification given.)

to bring about the same set of conditions; namely, excessive surface drag relative to the movement of the core.

The retarding forces may be several, the four principle ones known to produce this effect being:

1. Too obtuse a die angle.
2. A clogged die (which is in effect the same as No. 1).



FIG. 2.—CROSS-SECTION OF ROD FROM WHICH THE WIRE SHOWN IN FIG. 1 WAS DRAWN.

3. Incorrect ratios of carrier speeds (in the case of multiple-die machines) as compared with die ratios, making the supply of wire entering the die insufficient for the requirement of the carrier pulling on the emerging wire.

4. Excessive die friction due to faulty lubricating conditions or defective dies.

If the effect of such retarding forces becomes so great that the load on the emerging wire exceeds its limiting strength, the wire, of course, will break, but it often happens that a critical set of conditions may be temporarily set up which will cause a loading approaching, but not quite reaching, the maximum load the wire can withstand. Under these conditions the core will fail in the portion of the wire lying in the die itself while the external portion is supported by the pressure of the die walls. (See Fig. 3.)



FIG. 3.—LONGITUDINAL SECTION OF BRITTLE COPPER WIRE, SHOWING "CUP AND CONE" BREAK AND FRACTURED CORE.

In the case of steel wire, segregation may also be a cause of a very similar type of brittleness produced by cracking caused by lack of ductility in the core. No instances have come to the author's attention of such segregation in electro-copper wire bars. The only impurity of any substantial amount is cuprous oxide, and physical considerations of the manner of its existence in molten and solid copper, its specific gravity, and the fact that the freezing point of the eutectic is only a matter of about 33° C. below that of pure copper, all preclude the possibility of segregation of this impurity under normal circumstances.

.048	.052	.053	.051	.051	.051
.057	.045	.042	.046	.048	.045
.037	.047	.053	.041	.048	.032
.032	.049	.042	.044	.041	.041
.025	.047	.042	.048	.047	.033
.038	.041	.040	.033	.044	.033

FIG. 4.—SECTIONAL DISTRIBUTION OF OXYGEN IN A CAST COPPER WIRE BAR.

To demonstrate this point, a section $\frac{3}{8}$ in. thick was cut from the middle of a 250-lb. wire bar, selected at random from stock, and after

the top edge had been removed for a depth of 3 mm. it was subdivided into 36 small cubes. The enrichment of Cu_2O at the surface is due to absorption of atmospheric oxygen while molten, after casting, and consequently should not be considered as segregated impurity. These cubes were heated for 3 hr. at 800°C . in a stream of hydrogen. The loss in weight of each cube after heating was considered, for the purpose of this experiment, as being essentially oxygen, and the amount expressed in percentage is shown in the appropriate place in each square in Fig. 3.

It will be seen that the oxygen is slightly lower around the sides and bottoms (on account of rapid dendritic growth in these portions of the section during solidification.) Apart from this, however, it is very consistently distributed throughout the section.

Hence the "cup and cone" brittleness in hard drawn copper wire cannot normally be ascribed to segregation of oxide in the center of the bar.

DISTRIBUTION OF TENSILE STRENGTH IN HARD DRAWN COPPER WIRE

It is a well known fact that the maximum tensile strength that can be obtained in a given sample of hard drawn copper wire is dependent largely on the diameter of that wire. In other words, it is impossible to obtain more than a certain maximum strength for any given size regardless of the amount of cold work on the material. The values for various sizes of wire are plotted logarithmically in Fig. 5. After about 60 or 70 per cent. of cold reduction, the wire appears to acquire a tensile strength that is more or less consistent for a given size; for example, if soft rod 1 in. in diameter is drawn down to hard wire 0.1 in. in diameter and soft wire of 0.1 in. in diameter is drawn down to hard wire of 0.01 in. in diameter, the percentage of reduction will be identical, and since the tensile strength of the original stock is substantially the same in both cases, one would naturally expect the strength of the final products to be comparable when expressed in pounds per square inch, the hardening effect of cold work being a function of the amount applied. In actual fact, however, the finer size will have a considerably higher tensile strength per unit area than the coarser wire.

An explanation of this phenomenon has been put forward; namely, that the strength of cold-drawn wire lies principally in the outer layers and that since the ratio of surface to area varies inversely as the diameter, it would seem that there is a relatively larger amount of "skin" present compared to cross-sectional area as the diameter of the wire becomes smaller.

Another interesting phenomenon in connection with hard drawn wire is that which takes place when such wire is bent over a cylinder of small diameter. In view of the hardening effect of cold work, it would seem reasonable to assume that with such bending and consequent distortion

of the structure, if any change took place it would be in a direction tending to increase the tensile strength of the wire. Instead, however, it actually lowers the strength markedly to the accompaniment of an increased elongation value. This is known to the wire drawer as "break-

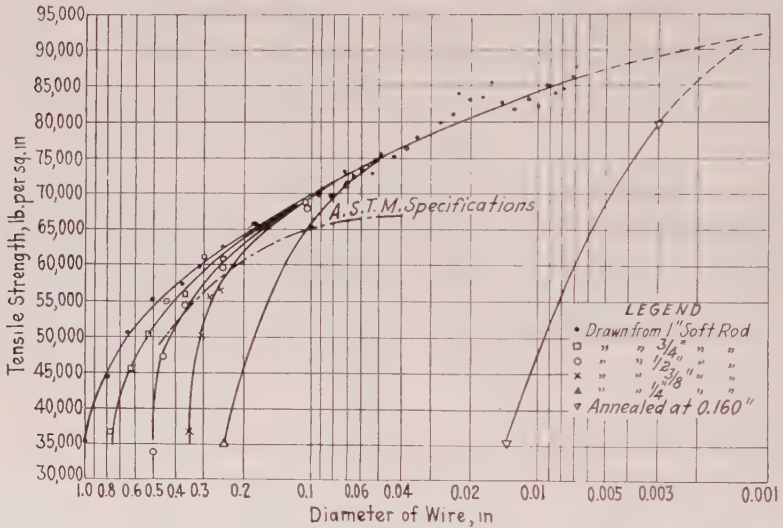


FIG. 5.—GRADUAL INCREASE IN TENSILE STRENGTH PER SQ. IN. WITH DECREASE IN DIAMETER OF WIRE. (CHART PLOTTED LOGARITHMICALLY.)

ing the back" of a wire. It is an apparent softening, which might be likened to a slight relief of strain by a light annealing operation, and the amount of the "breaking" varies with the amount of bending to which the wire is subjected.

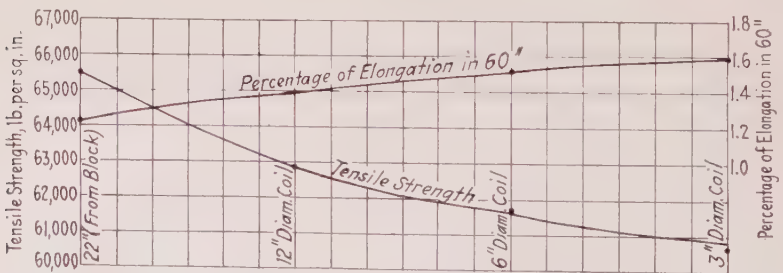


FIG. 6.—INFLUENCE OF DIAMETER OF COIL ON TENSILE STRENGTH AND ELONGATION OF 0.114-IN. HARD DRAWN COPPER WIRE.

Fig. 6 shows the effect of bending a wire of 0.114 in. diameter over cylindrical forms of diameters varying from 12 to 3 in. The drop in tensile strength with decrease in diameter of coil, and the corresponding increase in elongation, will be noted.

Because of this effect, it is obvious that strength can easily be lost if wire is drawn over a small block, or if it is subjected to the bending action of a sheave or guide wheel, on emerging from the final die of a wire-drawing machine. In practice, advantage is taken of this effect in the manufacture of Commercial Medium Hard Wire, and a very considerable degree of softening can be obtained by running the wire over pulleys of small diameter prior to laying it on the block. Experiments indicate that when the diameter of the block exceeds about 250 times the diameter of the wire, its influence on the tensile strength of the resultant product ceases to be noticeable.

Following this "skin hardness" theory to its logical conclusion, it would appear that in an extremely fine wire, where the skin-to-area ratio would be very high, one might expect the tensile strength to approximate that of the skin itself, and thus by testing such extremely fine wires it might be possible to obtain a measure of this value.

Unfortunately practical considerations make such tests somewhat unreliable, as microscopic imperfections, the problem of gripping the test pieces, and of obtaining apparatus of sufficient sensitivity for tests involving small fractions of an ounce, all have a pronounced influence on the value of the results obtained.

There is another method, however, of obtaining a measure of this skin strength, and one which has the added advantage of enabling the strength of any desired part of the section to be obtained. This method has been adopted in the present investigation. It consists of a gradual removal of the outer layers of metal by solution in acid, with tests of the wires at each successive stage in the process. By making many such tests, the tensile strength of each size can be found, and from these values the strength of the portions successively removed may be deduced by a simple process of subtraction.

In spite of expectation to the contrary, the action of the solvent does not produce pitting unless the strength is great enough to cause too rapid an action. With a 10 per cent. solution of nitric acid in water, which was used in these experiments, the action is quite gentle. The diameter of a 0.114-in. wire was reduced approximately 0.001 in. per hour in the larger sizes, and more rapidly as the wire became thinner.

A 5-gal Pyrex jar was used as a container, the wires being cut about 18 in. long, bent over at one end to form a small hook and suspended vertically in the acid from cross wires. In this way, 100 wires could be accommodated in one batch, and a sufficient amount of acid was used so that the strength was not reduced materially in less than 12 hours.

Experiments were conducted principally on 0.114-in. hard drawn copper wire, that being a size of general interest, but tests on other sizes were also made as the results of the preliminary work began to show some interesting possibilities. It was not practicable to continue acid attack

beyond about 0.030 in. diameter, as the wires lacked uniformity of section below this point. The results of the first series of tests are shown in Table 1.

TABLE 1.—*Tests of Tensile Strength in 0.114-in. Hard Drawn Copper Wire*

(FIRST SERIES)						
Mean Diam., In. after acid attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Pounds per Sq. In.
0.1129	0.01002	65,780 ^a	660			
0.1036	0.00843		554	106	0.001590	66,600
0.0928	0.00677		466	88	0.001660	53,000
0.0847	0.00564		388	78	0.001130	69,200
0.0737	0.004235		298	90	0.001405	64,100
0.0615	0.00297		227	71	0.001265	56,200
0.0509	0.002042	70,075 ^b	140	87	0.000928	93,400
0.0453	0.001614		113	27	0.000428	63,800

^a Average of the whole section.

^b Average of the residual core.

From the data obtained it has been possible to calculate the tensile strength of each zone removed by the acid. The values have been plotted in Fig. 7, the height of each column being a measure of the tensile strength of that portion of the wire, and the width indicating the amount of metal removed in each case. The broken line shows the average tensile strength of the whole wire. In this way a picture is obtained of the strength distribution in the whole section.

The outer skin of this wire is slightly above the average for the whole section in tensile strength—i. e., 66,600 lb. per sq. in. as compared with 65,780 lb. per sq. in.—but the residual core is considerably higher at 70,075 lb. per sq. in.

A striking result in this series is the extremely high zone between diameters 0.0615 and 0.0509 in., the latter having a tensile strength of 93,400 lb. per sq. in. Since this result was the mean of 10 tests, all of which were within a few pounds of each other, it hardly seems likely that it is a freak value. As will be seen in later tests, there is always a tendency for a high value at this point in the wire but nothing quite so high was reached in subsequent experiments.

The core in this series of tests was not dissolved away to such a small diameter as in the succeeding ones; consequently the value 70,075 lb. per sq. in. is a mean figure for the whole residual section, and by analyzing

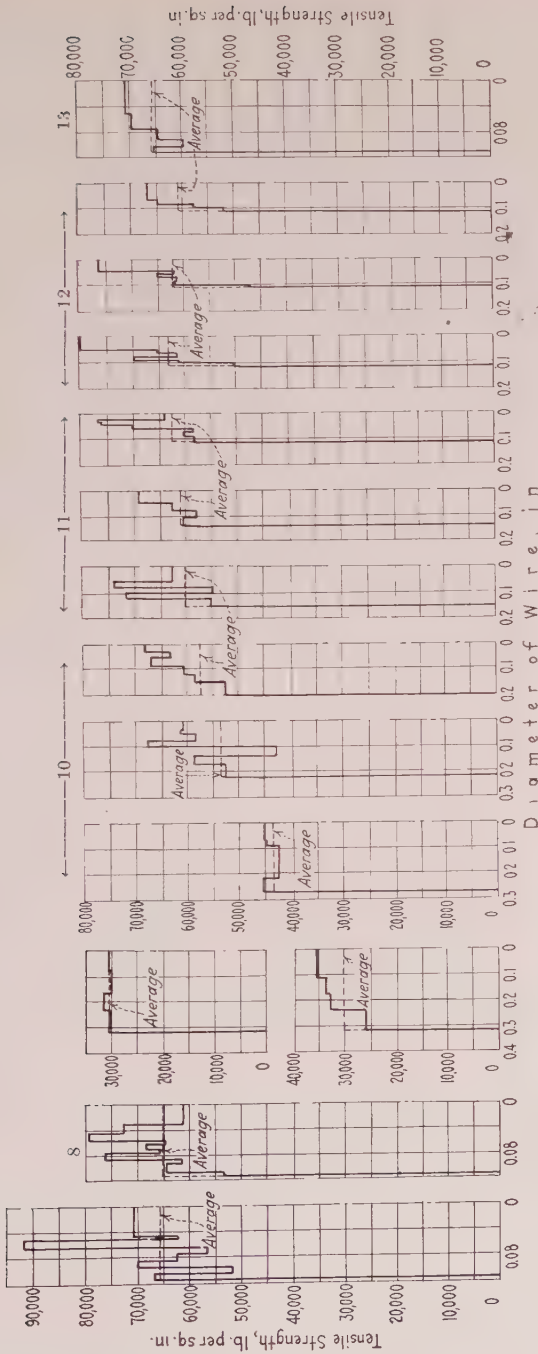


FIG. 7.—DISTRIBUTION OF TENSILE STRENGTH IN 0.114-IN. HARD DRAWN COPPER WIRE (FIRST SERIES).

FIG. 8.—DISTRIBUTION OF TENSILE STRENGTH IN $\frac{5}{16}$ -IN. ROD, (UPPER) AS HOT-ROLLED AND ANNEALED, AND (LOWER) AS ROLLED.

FIG. 9.—DISTRIBUTION OF TENSILE STRENGTH IN 0.114-IN. HARD DRAWN COPPER WIRE (SECOND SERIES).

FIG. 10.—EFFECT OF SUCCESSIVE DRAFTS ON TENSILE STRENGTH DISTRIBUTION IN HARD DRAWN COPPER WIRE; (LEFT) FIRST DRAFT (0.312-0.262 in.); (CENTER) SECOND DRAFT (0.262-0.222 in.); (RIGHT) THIRD DRAFT (0.222 TO 0.185 in.).

FIG. 11.—EFFECT OF SUCCESSIVE DRAFTS ON TENSILE STRENGTH DISTRIBUTION IN HARD DRAWN COPPER WIRE; (LEFT) FOURTH DRAFT (0.185-0.145 in.); (CENTER) FIFTH DRAFT (0.145-0.127 in.); (RIGHT) SIXTH DRAFT (0.127-0.114 in.).

FIG. 12.—EFFECT OF BENDING INTO COILS OF SMALL DIAMETER; DISTRIBUTION OF TENSILE STRENGTH IN 0.114-IN. HARD DRAWN COPPER WIRE; (LEFT) 12-IN. DIA. COIL; (CENTER) 6-IN. DIA. COIL; (RIGHT) 3-IN. DIA. COIL.

FIG. 13.—EFFECT OF REVERSAL IN DIRECTION OF DRAWING AT LAST DIE; DISTRIBUTION OF TENSILE STRENGTH IN 0.114-IN. HARD DRAWN COPPER WIRE.

the core still further it can be shown that there are considerable variations of strength in this portion.

It will also be noted that apparently there is a progressive increase in strength up to a maximum of 93,400 lb. per sq. in. and then a falling off. The actual strength at the axis of the wire becomes a matter of conjecture but the indication is that it might be low, the point of maximum strength apparently lying about midway between the outer skin and the axis.

In order to check these interesting results, another series of tests was made on another coil of 0.114-in. wire, taking 10 tests as before from each die; this time dissolving the wire to about 0.030 in. and thus obtaining a truer picture of the conditions in the core. Results are shown in Table 2 and are plotted in Fig. 8.

TABLE 2.—*Tests of Tensile Strength in 0.114-in. Hard Drawn Copper Wire*

Mean Diam., In. after Acid Attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.1128	0.01000	66,000	660			
0.1058	0.00878		594	66	0.00122	54,200
0.0916	0.00658		452	142	0.00220	64,500
0.0849	0.00566		395.5	56.5	0.00092	61,400
0.0791	0.00492	61,100	339	56.5	0.00074	76,400
0.0703	0.00388		271	68.0	0.00104	65,400
0.0613	0.00295		207.5	63.5	0.00093	68,300
0.0565	0.00251		179	28.5	0.00044	64,700
0.0450	0.00159		105	73.2	0.00092	79,500
0.0330	0.000856		52.3	53.5	0.00734	72,800

The results in the second series of tests are not in strict agreement with the previous ones. The strength of the inner core is below the average for the whole section and the outer skin is considerably lower. The general trend, however, is somewhat similar; namely, an increase from the outside to a point about midway between the outer skin and the axis.

An explanation of the difference between the two series of tests probably lies in the fact that too much metal was dissolved away from the outer skin in the first case, and possibly the extreme skin would have been actually weaker than shown if a thinner portion had been examined. The results of both series of tests, however, are in contradiction to the theory that the highest tensile strength of a wire lies in the skin.

EXAMINATION OF HOT-ROLLED ROD

It was thought possible that the structure of the rods from which the above wires were drawn might show somewhat similar properties on a less exaggerated scale, therefore tests were next made on such material.

Samples of $\frac{5}{16}$ -in. hot-rolled rod were selected from stock and treated in acid, as described. Simultaneous tests were also made with $\frac{5}{16}$ -in. hot-rolled rod which had been previously annealed to remove all residual strains. The values obtained are given in Tables 3 and 4 and are plotted in Fig. 9.

TABLE 3.—*Distribution of Tensile Strength in Commercial Hot-rolled $\frac{5}{16}$ -in. Copper Rod*

Mean Diam., In. after Acid Attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.3125	0.0768	30,900	2,367			
0.2325	0.0424		1,455	912	0.0344	26,500
0.1675	0.0220		766	689	0.0204	33,800
0.1115	0.0098	35,550	347	419	0.0122	34,200

TABLE 4.—*Distribution of Tensile Strength in Commercial Hot-rolled $\frac{5}{16}$ -in. Copper Rod Annealed at 1000° F. for One Hour*

Mean Diam., In. after Acid Attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.312	0.0764	30,700	2,350			
0.206	0.0333		1,025	1,325	0.0431	30,700
0.158	0.0196		593	432	0.0137	31,500
0.083	0.0054	30,600	166	427	0.0142	30,100

The results indicate unmistakably that the distribution of strength is not perfectly uniform in the commercial rod, whereas in the annealed samples there is an almost negligible divergence from the straight line at any point in the section, as might be expected.

In the commercial rod, a contour can be observed which is somewhat similar to that in the hard drawn wire, and this fact appears to add some weight to the contention that rods finished at a low temperature and left with a certain amount of internal strain produce a somewhat stronger wire than do annealed rods, although it is admittedly difficult to understand how such a small amount of cold work can have much influence as compared with the effect of seven or eight reductions through dies.

EFFECT OF SUCCESSIVE DIES IN COLD DRAWING FROM $\frac{5}{16}$ -IN. ROD TO 0.114-IN. WIRE

The next investigation consisted in studying the manner in which the tensile strength gradually increases in successive drafts. The rod was

TABLE 5. *Distribution of Tensile Strength in Hard Drawn Copper Wire during Reduction from $\frac{5}{16}$ -in. Rod to 0.114-in. Wire*

First Die						
Mean Diam., In. after Acid Attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.271	0.0577	43,500	2,512			
0.219	0.0376		1,600	912	0.0201	45,400
0.094	0.0069		311.7	1,288.3	0.0307	42,200
0.0735	0.0042	44,700	191.2	120.5	0.0027	44,500
Second Die						
0.222	0.0386	53,900	2,087			53,900
0.172	0.0233		1,267	820	0.0153	53,500
0.142	0.0158		837	430	0.0075	57,200
0.102	0.0081		508	329	0.0077	43,000
0.983	0.0054		322	186	0.0027	69,000
0.052	0.0021		130	192	0.0033	58,300
0.036	0.00102	60,800	62	68	0.00108	62,800
Third Die						
0.192	0.0289	57,200	1,650			
0.151	0.0179		1,079	57.1	0.0110	52,000
0.1219	0.0108		719.3	359.7	0.0071	50,800
0.0899	0.0063		399.6	319.7	0.0045	71,000
0.046	0.0016		105	294.6	0.0047	62,600
0.035	0.00095	60,800	65	40.0	0.00065	61,600
Fourth Die						
0.1545	0.0187	60,500	1,131			
0.1237	0.0121		758	373	0.0066	56,900
0.1030	0.0083		496	262	0.0038	68,000
0.0764	0.0046		307	187	0.0037	50,400
0.0593	0.0027	62,300	173	134	0.0019	70,500
Fifth Die						
0.1362	0.0145	61,000	889			
0.1013	0.0081		500	389	0.0064	60,500
0.0795	0.00472		321	179	0.00348	62,200
0.0446	0.00156	60,800	108	213	0.00316	67,000
Sixth Die						
0.114	0.0101	65,000	662			
0.0893	0.006		414	24.8	0.0041	60,500
0.0725	0.0041		282	132	0.0022	60,000
0.065	0.0034		241	41	0.0007	58,500
0.0443	0.00155		112	129	0.00185	69,500
0.0363	0.00104		73	39	0.00051	76,500
0.0273	0.00058	64,000	37.3	35.7	0.00046	77,000

drawn down cold on a single 22-in. block in six reductions, using the following die set-up:

(0.312-in. rod) — 0.270 — 0.222 — 0.185 — 0.145 — 0.127 and 0.114 in.

A quantity of wire was taken at each stage in the reduction, sufficient for 50 or 60 samples and the same process of physical analysis as before was carried out. The results are given in Table 5 and shown diagrammatically in Figs. 10 and 11. *

It will be seen that as the wire becomes harder it adopts a similar contour of tensile strength to that shown in the previous tests. The one exception is the wire after the first draft, in which the tensile strength is highest in the skin. This is to be expected, since the cold work of the die has not yet completely penetrated to the soft core. After the second draft, however, the effect of the cold work appears to be more marked on the core than on the outer layers.

EFFECT OF BENDING HARD DRAWN WIRE INTO COILS OF SMALL DIAMETER

Reference has already been made to the effect of bending hard drawn copper wire, and it has been shown that the smaller the diameter of the coil, the more the tensile strength is reduced until a minimum is reached. An explanation that is usually offered to this phenomenon is that the skin is in some way broken up, and on the theory that the strength is really concentrated in this skin anything that in any way injures it would lower the strength of the wire as a whole.

The experiments described above, however, would indicate that the strength does *not* lie in the skin and consequently there must be some other explanation to the phenomenon. As a further experiment, therefore, a physical analysis was made on wire which had been bent over cylinders of 12, 6, and 3-in. diameters respectively. The results are shown in Table 6 and plotted in Fig. 12.

It will be seen that there is a gradual evening-up effect as the wire is bent into smaller and smaller coils. On the 12-in. coil the core is by far the highest portion, whereas in the 3-in. coil there is less variation in strength at any point in the section with the exception of the extreme outer skin. There is still, however, a tendency for a gradual increase in strength from skin to core.

TABLE 6.- *Effect of Coil Diameter on Tensile Strength Distribution in 0.114-in. Hard Drawn Copper Wire*

Twelve-inch Diameter Coil						
Mean Diam., after Acid Attack	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Pounds	Diff. in Load, Pounds	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.1139	0.01021	62,875	641			
0.1004	0.00793		529	112	0.00228	50,000
0.0893	0.00627		428	101	0.00166	60,800
0.0777	0.00474		333	93	0.00153	60,700
0.0710	0.00396		281	54	0.00078	69,200
0.0580	0.00264	80,020	201	80	0.00132	60,600
0.0503	0.00199		159	42	0.00065	64,600
Six-inch Diameter Coil						
0.11358	0.01013	61,775	626			
0.09895	0.00769		511	115	0.00244	47,200
0.08220	0.00532		365	146	0.00237	61,500
0.0708	0.00393		280	85	0.00139	61,200
0.06025	0.00285		210	70	0.00108	64,800
0.054	0.00233	76,400	178	37	0.00052	61,500
Three-inch Diameter Coil						
0.1134	0.01002	60,500	606			
0.0948	0.00707		453	153	0.00295	51,800
0.0861	0.00582		381	72	0.00125	57,600
0.0693	0.00377		249	132	0.00205	64,400
0.0611	0.00293	66,580	195	54	0.00084	64,300

EFFECT OF REVERSAL IN DRAWING DIRECTION

As a final experiment, the effect of reversing the direction of draw in the last die was studied. A $\frac{5}{16}$ -in. rod was drawn down to 0.122-in. diameter in a continuous machine and then drawn down to 0.114-in. diameter in one draft on a single block in the reverse direction. In other words, the trailing end of the coil from the continuous machine was made the leading end in the final draft. In this way, the direction of surface flow was reversed.

A physical analysis was made of the strength distribution as before, the values of which are given in Table 7 and plotted in Fig. 13.

The strength of the wire as a whole was increased slightly over that of wire drawn in one direction throughout although the increase was not

marked. It is a generally accepted fact that wire drawn on a single block usually has somewhat greater strength than that drawn on a continuous machine and possibly this is due to the effect of reversal in drawing direction, since the direction is reversed at each step when drawing one die at a time.

TABLE 7.—*Effect on Strength Distribution in 0.114-in. Hard Drawn Copper Wire when Direction of Drawing is Reversed at Last Die*
Drawn to 0.122-in. on Continuous Machine. Drawn from 0.122 to 0.114-in. on Single Block in Reverse Direction

Diam., In.	Area, Sq. In.	Tensile Strength, Lb. per Sq. In.	Actual Load, Lb.	Diff. in Load, Lb.	Area of Dissolved Portion, Sq. In.	Tensile Strength of Dissolved Portion, Lb. per Sq. In.
0.1164	0.01065	66,310	706			
0.1013	0.00807		538	168	0.00258	65,200
0.0928	0.00677		461	77	0.00130	59,200
0.0716	0.00403		284	177	0.00274	64,600
0.0549	0.00237	71,000	168	116	0.00166	69,900

In the present case, there appears to be an undoubted increase in tensile strength at the skin as compared with the wire shown in Fig. 8. The strength of the core, however, still shows a value above the average for the whole wire, and from this it would be inferred that the reversal has not had a very marked effect.

MICROSCOPIC STUDY OF HARD DRAWN WIRE STRUCTURE AT DIFFERENT POINTS IN THE SECTION

It was thought that a study of the microscopic structure of hard drawn copper wire at various points in the cross-section might reveal some differences corresponding to the areas of high and low tensile strength shown in the above experiments, either by a change in orientation or in the number of slip planes in the individual crystals. A complete and exhaustive traverse was made across the diametrical section of a 0.114-in. diameter hard drawn wire in several places, each area being photographed at 750 diameters, so that when placed side by side the photomicrographs of the wire gave a composite picture of approximately 85 in. long.

Contrary to expectations, there was no essential difference observed in the crystal structure at any point in the section, each photomicrograph showing similarly oriented crystals greatly distorted and broken up along innumerable slip planes. To avoid repetition, only three of these photomicrographs are shown in Fig. 14; representing a point on the outer skin,



FIG. 14.—HARD DRAWN COPPER WIRE. $\times 750$. *a*, STRUCTURE NEAR OUTER SKIN. *b*, STRUCTURE MIDWAY BETWEEN SKIN AND CORE. *c*, STRUCTURE AT CORE.

15



16



FIG. 15.—OVER-STRAINED HARD DRAWN COPPER SHOWING INTRACRYSTALLINE CRACKS. $\times 3000$.

FIG. 16.—NORMAL HARD DRAWN COPPER WIRE, SHOWING HIGHLY DISTORTED CRYSTAL STRUCTURE WITH NUMEROUS SLIP-PLANES. $\times 3000$.

(Reduced to $\frac{2}{3}$ original scale, original magnifications given.)

one midway between the skin and the core, and one at the core itself, respectively. The similarity in the three structures is readily seen.

A study was also made of the structure of the brittle 0.114-in. diameter wire, to which reference was made in an earlier portion of the paper, shown in Fig. 4. Minute cracks were observed at many points in the section in addition to the major fracture at the core itself. Fig. 15 shows one of these small fractures about midway between the skin and the core of this wire.

Some interesting studies were also made at higher magnifications and Fig. 16 shows a photomicrograph of a core of a 0.114-in. hard drawn wire. The slip planes and highly distorted structure are very noticeable. A rough calculation will show that there are approximately 50,000 of these planes to the linear inch. Assuming that there were about 1000 crystals to the linear inch in the original soft rod, it will be seen that each crystal apparently developed about 50 slip planes.

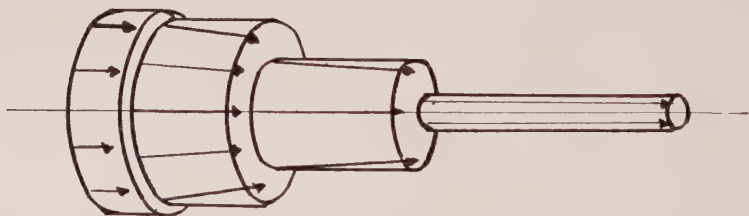


FIG. 17.—DIRECTION OF PREFERRED ORIENTATION OF CRYSTALS IN HARD DRAWN WIRE, AS SHOWN BY X-RAY ANALYSIS.¹

Although microscopic evidence does not reveal any marked change in orientation, X-ray methods have shown that such changes exist. An interesting article was recently published on this subject by Schmid and Wassermann.¹ These authors show that a "preferred orientation" is produced by cold working, and in metals like copper, aluminum, gold and silver, whose lattice is of the face-centered variety, there can be two different arrangements of the crystal axis, either the diagonal or one of the edges of the elementary cubes tending to arrange itself parallel to the axis of the wire.

The X-ray study also brings out the interesting fact that this tendency for preferred orientation in a direction parallel to the axis is most marked at the center of the wire. In the outer layers, the crystal orientation tends to point inward in the direction towards which the wire has been drawn, and at an angle corresponding approximately to that of the die wall. This tendency becomes more marked as the outer skin is

¹ *Zeitschr. für Metall* (August, 1927) 325.

approached but at the skin itself the orientation is less marked and the crystals again tend to lie parallel to the axis.

The diagram in Fig. 17 is reproduced from their paper to illustrate these facts. Four layers of a wire are shown and the arrows indicate the direction of preferred orientation in each layer. Furthermore, the length of the arrows indicate approximately the degree to which the tendency towards preferred orientation manifests itself.

By making tensile tests of each area, in a manner similar to that described in the present paper, it is interesting to note that they find a progressive increase in strength from the skin to the core of a hard drawn wire and thus in general confirm the author's investigations.

SUMMARY AND CONCLUSION

In this investigation, various types of copper rod and hard drawn wire have been treated in dilute nitric acid in such a manner as to remove successive layers of metal from the surface. By testing batches of these after varying periods of immersion in acid, it has been possible to obtain a measure of the tensile strength of different portions of the sections. These have been plotted diagrammatically.

The results of the experiments show that the strength of hard drawn wire and commercial hot-rolled rod is by no means constant throughout the section. The "skin" of the wire is, in general, below the average for the whole. There appears to be a point of low strength at the axis, but the method of testing adopted does not permit complete exploration of this area.

The region of highest strength appears to be in a zone near the core.

Commercial hot-rolled rod shows a variance of strength throughout the section, being lowest at the outer zone and highest at, or near, the core. Annealed rod, however, is almost uniform throughout.

The effect of one draft on commercial soft copper rod is to raise the strength of the skin above the average for the whole wire. Further drafts bring about the same conditions as before.

The effect of bending a hard drawn wire into a small coil is to lower the average strength and develop a more uniform condition throughout.

When wire is drawn continuously in one direction to the penultimate die, and then the drawing direction reversed in the final die, the result is an increase in skin strength, the remainder of the section being unchanged.

While X-ray studies have been shown to reveal a "preferred orientation" of the crystals at various points in the section of a hard drawn wire, microscopic studies do not show any essential change in crystal structure at any point, corresponding to zones of high and low tensile strength.

Two common causes of defective wire are discussed; namely, laminations and overdrawing.

DISCUSSION

H. F. MOORE, Urbana, Ill.—During the past year there have been carried on, in the materials testing laboratories of the University of Illinois, metallographic studies of cracks in copper caused by repeated stress.² The structure, or rather the break-up of structure, was quite similar to that shown by the author. There seemed to be a tendency, though not a very well marked tendency, for fatigue marks to follow the planes of cleavage in the copper.

In previous experiments it has been found³ that the fatigue strength of cold-drawn copper is but little, if any, above the fatigue strength of cold-drawn copper subsequently annealed. It is also general experience that too drastic cold rolling of either copper or steel actually reduces the strength. In the process of cold working there seem to be two effects; one a beneficial effect which is associated with intracrystalline slip, and the other a destructive effect associated with the formation of minute cracks.

In their initial stages, minute cracks formed under repeated stress are too fine to be seen even with the modern microscope. At the present time X-ray spectroscopic analysis can give us some notion of the general "statistical" behavior of the atoms in a mass of metal, but cannot tell us much, if anything, about the details of fracture of atomic bonds. The problem of the initial stages of progressive fracture, in my opinion, lies in a field between that of the microscope and that of the study of atomic structure. This paper is welcome as a contribution to the study of this problem.

F. H. CLARK, New York, N. Y. (written discussion).—The studies carried out by Mr. Harris on "cup and cone" brittleness, as shown in Fig. 3, are of great interest to the writer, as instances of failure which appear to be identical have been found in wire purchased by the Western Union Telegraph Co. After a careful reading of his text, it is not clear to the writer whether Mr. Harris believes this type of failure is ever due to the presence of impurities in the copper or whether it is always due to mechanical effects in the drawing operation.

The writer has had occasion to investigate instances of failure which have occurred during the unreeling operation and installation of copper wire for telegraph service. These failures invariably show a "cup and cone" fracture.

Tests made on coils containing the defective wire show low tensile strength and low elongation. The writer has examined under the microscope samples of such failures and has always found large quantities of cuprous oxide at these breaks. The oxide observed exceeded the amount normally found in hard-drawn copper used for electrical purposes.

Fig. 18 of Specimen No. 1 shows a longitudinal section of copper wire at 5 dia. magnification with a "cup" fracture. Three other crescent-shaped areas are visible. Fig. 19 shows one of these areas at 100 dia. Distortion of the copper grains is visible. The dark spots of oxide reveal their characteristic bluish tint under the microscope. Figs. 20 and 21 show portions of the same area as Fig. 19 but the magnification is 1000 diameters.

Fig. 22 of Specimen No. 2 shows segregation in a cone-shaped structure. Fig. 23 at higher magnification proves this to be an excessive amount of cuprous oxide.

Fig. 24 shows a crack as shown in Fig. 25. It will be noted that the crack runs across the wire at right angles to the direction of drawing. The path of the crack

²H. F. Moore and F. C. Howard: Metallographic Study of the Path of Fatigue Failure in Copper. Eng. Exp. Sta., Univ. of Ill. *Bull.* 176 (1928).

³H. F. Moore and T. M. Jasper: An Investigation of the Fatigue of Metals. Eng. Exp. Sta., Univ. of Ill. *Bull.* 152 (1925).



↑
See Fig. 19.

↑
Fracture

FIG. 18.—SPECIMEN NO. 1. COPPER WIRE NO. 8 B. W. G. CUP FRACTURE AND CRESCENT MARKINGS IN DEFECTIVE COPPER WIRE. $\times 5$.



↑
See Fig. 20.

↑
See Fig. 21.

FIG. 19.—ONE OF CRESCENT-SHAPED STRUCTURES OF FIG. 18. $\times 100$.

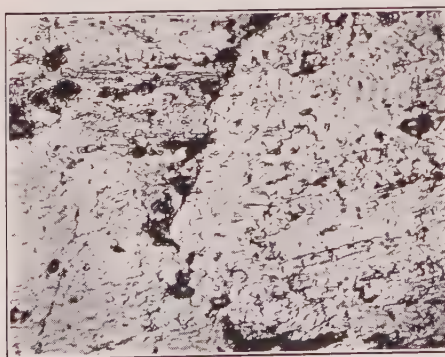


FIG. 20.—ONE OF CRESCENT-SHAPED STRUCTURES OF FIG. 18. $\times 1000$.
(Reduced to $\frac{1}{2}$ original scale, original magnification given.)

leads from one inclusion of oxide to the next. All samples of copper were etched with ammoniacal peroxide.



FIG. 21.—CUPROUS OXIDE IN CRESCENT-SHAPED STRUCTURE. $\times 1000$.
(Reduced to $\frac{1}{2}$ original scale, original magnification given.)



↑
See Fig. 23.

FIG. 22.—SPECIMEN NO. 2. COPPER WIRE NO. 8 B. W. G. CRESCENT-SHAPED BODY. $\times 100$.

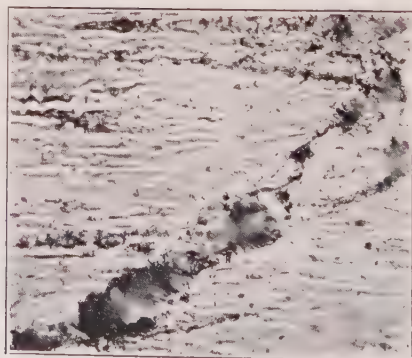


FIG. 23.—CUPROUS OXIDE IN CRESCENT-SHAPED BODY OF FIG. 22. $\times 1000$.
(Reduced to $\frac{1}{2}$ original scale, original magnification given.)

The writer believes that cuprous oxide does segregate in hard-drawn copper wire and produces brittleness with subsequent failure. In the writer's experience, the "cup and cone" brittleness and crescent-shaped structures have always been associated with cuprous oxide.

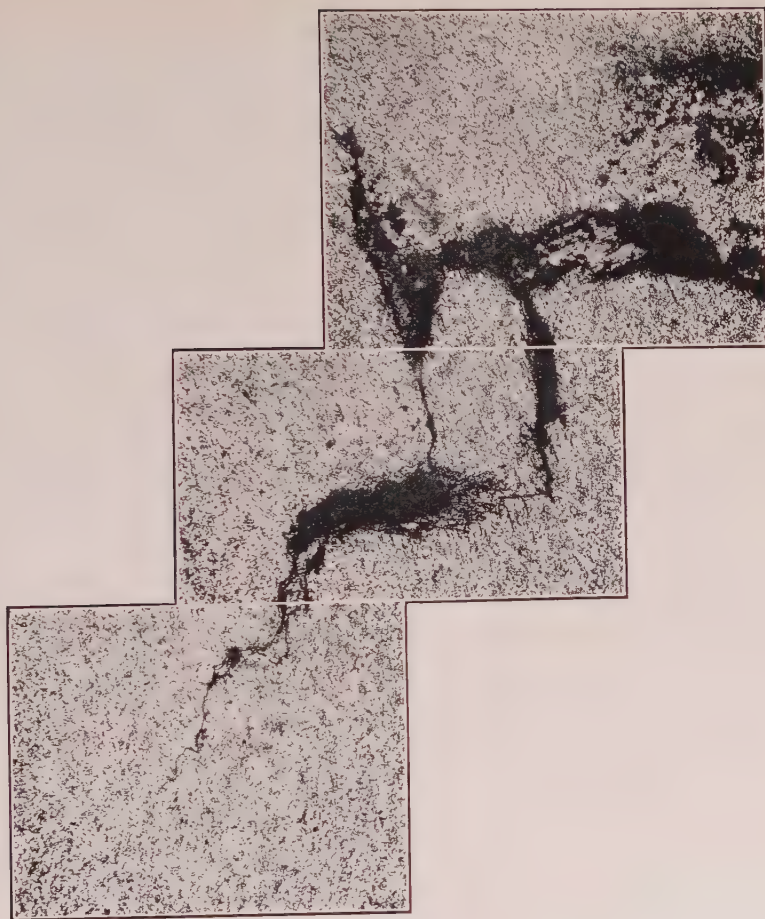


FIG. 24.—SPECIMEN NO. 3. COPPER WIRE NO. 8 B. W. G. TRANSVERSE CRACK FORMED WHEN WIRE WAS BENT. CRACK FOLLOWS CUPROUS OXIDE INCLUSIONS. COPPER GRAINS SLIGHTLY ANNEALED DUE TO MOUNTING SAMPLE IN ZINC FOR POLISHING. $\times 100$.
(Reduced to $\frac{1}{2}$ original scale, original magnification given.)

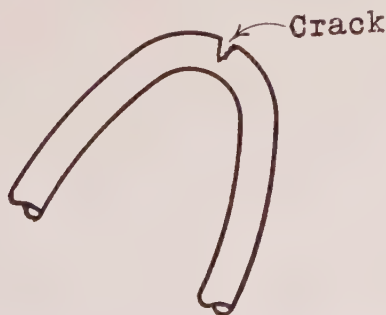


FIG. 25.—SKETCH OF SECTION OF WIRE SHOWING POSITION OF CRACK SHOWN IN FIG. 24

F. W. HARRIS (written discussion).—In reply to Dr. Clark's discussion, I would state that my belief is that "cup and cone" brittleness is essentially a mechanical phenomenon, the main causes of which are outlined in the second and third pages of the paper. The principal reasons for this opinion are:

1. Cuprous oxide does not migrate on solidification in such a manner as to cause any segregation such as is claimed to have produced the brittleness shown in Dr. Clark's examples. The possibility of wire of high oxide content also possessing "cup and cone" brittleness is not denied, but I would suggest that such oxide in itself is not the prime cause of this peculiar type of brittleness.

2. This brittleness can be produced at will from otherwise normal material by arranging the drawing conditions in such a way as to produce excessive surface friction.

3. The uniformity of spacing of the fractures throughout the length of the wire rather belies any segregation explanation, and suggests that a periodic vibration is set up as the core of the wire breaks.

The large inclusions shown in the fracture in Fig. 7 would appear to be cupric oxide scale, rather than cuprous oxide eutectic, on account of their jagged nature, and have apparently been forced in from the surface. When seen through a microscope equipped with the usual vertical illumination, both cuprous and cupric oxides appear blue, but under oblique illumination, cupric oxide appears blue-black, and cuprous oxide a rich ruby color. This is a useful test in such cases.

E. M. WISE, Bayonne, N. J.—The curves shown for the change in strength after removing various amounts of the surface of the wire are strongly indicative of high internal stresses in the wire. I would like to ask the author whether measurements were made of the change in length of the wire after removing varying amounts of the surface material. It seems probable that part of the change in strength observed is due to a variation in the direction and magnitude of the stresses in the outer layers of the wire.

W. B. PRICE, Waterbury, Conn.—Is there not a possible explanation in the tensile strength between the outer layer and the inner layer due to self-annealing of the wire? It is particularly significant in the closer packed coils, and if you remove the outer skin, you get in the center the real tensile strength of the wire. I think it is also very significant that on the thoroughly annealed wire the physical properties are practically constant and it may be that it is annealed at such a low temperature it is not resolved by the microscope.

There have been instances of copper that have shown annealing and even burning at very low temperatures. I think Mr. Bassett once told me it happened in the neighborhood of 160° C.

D. K. CRAMPTON, Waterbury, Conn.—The reference to internal stresses interested me. I was struck with the similarity of the shape of the curves of distribution of tensile strength with similar curves of distribution of internal stress on drawn rod and wire; that is, distribution of stress as measured by Heyn's method of removing surface layers and measuring increase in length.

I think probably there is some close connection between the two phenomena. As perhaps the first evidence of that, we all know that drawn rod or wire subsequently coiled has a more uniform distribution of stress than just as drawn. We see this distinctly in brass-mill practice and I see no reason why it should not hold also for copper.

F. E. CARTER, Newark N. J.—Some years ago, as I recall it, Heyn⁴ gave a method of determining strains in cold-rolled metals, using nickel-steel and copper alloys. He

⁴ *Jnl. Inst. Met.* (1914) **12**, 3.

cut concentric layers from the surface of the rod, accurately measuring the length after each operation. He was able in this way to measure the strain in the rod and I would be interested to know how the results given in the present paper agree with those given by Heyn.

F. W. HARRIS.—Mr. Wise's suggestion that variation in internal stresses should be accompanied by variations in length is of much interest. I did not actually make such measurements in the present study. It is largely a question of developing a satisfactory apparatus, as there are some obvious difficulties to be surmounted.

Mr. Price commented on the fact that the difference in stresses may be due to self-annealing during the drawing. There is little doubt that the influence of heat developed by friction during the passage of the wire through the die is an important underlying cause of many variations in the physical properties of wire.

W. B. PRICE.—Would not the outside anneal against the face of the die? Would not more heat generate there?

F. W. HARRIS.—No doubt very high temperatures may sometimes be developed locally, especially under conditions of high reduction and poor lubrication, but it might be argued that the coolest portion is the surface, due to the quenching action of the solution. On the other hand, if a steam film were developed, the reverse might be true. The thermal conductivity of copper being so high, it is certain that any pronounced temperature gradient in a small wire could not exist very long.

W. B. PRICE.—Several years ago Rawdon showed⁵ that in rolling very fine copper sheet there was pronounced softening. In the tests he used rolls which were not cooled with water and the softening was due to self-annealing in that case.

F. W. HARRIS.—I would think the conditions were so different in drawing the wire through solution as compared with rolling that the two could hardly be compared.

W. H. BASSETT, Waterbury, Conn.—It is possible that wire may come from a wire machine quite considerably annealed, in spite of the solution, and that is one of the things in high speed drawing that certainly has to be considered. As to the physics of the heating of the wire, one does not know, but it is true that the heat generated by the die is very considerable. Not only in wire machines, but in some other operations of drawing copper, it has been observed in certain drawing operations that the copper came through the die at a red heat on account of the amount of work that was done in reducing the section.

I might suggest for discussion at some other time—I do not know whether it belongs in this section or not—the physics of the drawing of metal through a die. It is quite possible to produce at will the broken center in wire by shaping the die. The shape of dies is a very important matter and has a very great deal to do with the properties of the metals that are drawn through the dies.

Whether Dr. Moore's remarks refer to the breaking apart of the crystals due to the tensile pull which would be, of course, unsupported by a die, or whether they refer to material which has been drawn through dies, I do not know, but the support which the metal receives from the die, the character of the die, the length of bearing, and so forth, are extremely important in the drawing of wire and in the drawing of rods, and are matters upon which a great deal of time and study might be well spent. I do not know of any publications on the subject. There may be some, but certainly the matter is worthy of study.

⁵ H. S. Rawdon and W. H. Mutchler: Effect of Severe Cold Working on Scratch and Brinell Hardness. *Trans.* (1924) **70**, 342.

G. A. Roush, Bethlehem, Pa. (written discussion).—In going over the various conditions and conclusions outlined by Mr. Harris, I cannot help feeling that the conclusions drawn in regard to the tensile strength of the various layers of the drawn wire cannot be entirely justified so long as they do not take into account the internal strains existing in the wire. There is no doubt about the existence of layers of varying tensile strength, and likewise of similar layers of varying strain, but the methods used by Mr. Harris cannot give one a true measure of the tensile strength because they do not take into account the accompanying strains, which may either increase or decrease the tensile strength, depending on whether the strain is tensile or compressive.

For simplicity in analyzing the conditions existing in a drawn wire of this kind, let us assume that it consists of only an inner core and a single surrounding layer, as shown in Fig. 26. As the wire aAa is drawn through the die it is constricted as shown in bBb , to emerge in an elongated form as $cC'c$. As the wire passes through the die the surface layer aa is subjected to heavy tensile stress and friction on the walls of the die, with the result that the surface layer cc of the drawn wire is under a severe tensile strain. At the same time, due to the constricting action of the die, there is a certain amount of lateral compression, but under the existing conditions the tensile stress

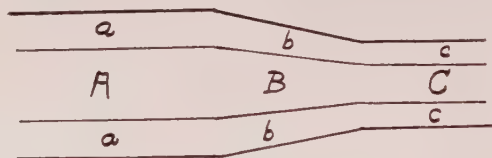


FIG. 26.

predominates over the compressive, so that at cc the metal is under considerable residual longitudinal tension. As the core A passes through the die it is also subjected to tension and compression, but here the heavy dragging friction of the walls of the die is absent, while at B the core is undergoing lateral compression due to the action of the die on the surface layer bb . Which of the strains thus set up predominates will depend on the combination of a number of conditions, the draft of the die probably being the most important. If this analysis of the conditions is correct, the surface cc is almost inevitably in longitudinal tension, but in the core C the original tension of the draw may or may not be counteracted by the compression. Let us then see where this argument leads us if followed along these two alternatives.

For this purpose assume the wire to be of a metal with a normal tensile strength of 60,000 lb. per sq. in., and assume the areas C and cc equal. With a heavily predominating tensile strain in cc , amounting say to 20,000 lb., the net strength of this section is then only 40,000 lb.; with a smaller predominating tensile strain in C , say of 10,000 lb., the net strength of this section would be 50,000 lb., or a combined strength of 45,000 lb. for the wire as a whole, and this is what the tensile test should show. If this wire were placed in acid and the layer cc removed, much of the strain in C , both tensile and compressive, would be relieved, and the core would, when tested alone, show the increased strength resulting from the relief from the strain. If C under these conditions tests 55,000 lb., an increase of 5000 lb. over its previous condition, this value when compared with the average value of 45,000 lb. for the whole wire would lead to the conclusion that the surface layer had a strength of only 35,000 lb., instead of 40,000 pound.

A similar discrepancy, but in the opposite direction, would result if the compressive strains prevailed in the core. Assume the same conditions as before in cc , but a compressive strain in C that predominates over the tensile; the magnitude of this strain is probably considerably less than the corresponding value in the preceding case, since

the compressive stress is applied laterally, and only such of the force as is resolved into longitudinal compression is applicable to reducing the opposing tensile stress, so that even though there should be a residual longitudinal compression, it is not likely to be large. If we assume this compressive strain to be 2000 lb., this with the normal 60,000 lb. will make a net strength of 62,000 lb., which, when averaged with the 40,000 lb. strength of *cc*, gives an average value for the whole wire of 51,000 lb. When the *cc* layer of this wire is dissolved in acid, the predominating strains in *C*, being small and radially compressive, will almost entirely disappear, leaving the metal with approximately its normal strength of 60,000 lb., which, when balanced against the average of 51,000 lb. for the entire wire, gives 42,000 lb. for the strength of *cc*, instead of 40,000 pound.

Therefore it seems quite probable that the values attributed by Mr. Harris to the various layers tested, as shown in Figs. 7 to 13, have been materially distorted by conditions similar to those outlined. Just how much variation from the true values one might encounter is largely dependent on the relations that happen to be struck between the thickness of the layers dissolved by the acid and the layers subjected to any particular strain. If *cc* were removed in two layers instead of one, the differences would be lessened by the decreased opportunity for the relief of the internal strains in *C* by the remaining half of *cc*. On the other hand, if the first layer removed took two-thirds of *cc*, and the second the remainder of *cc* and an equal amount of *C*, the differences would be increased.

It would seem necessary then, before dependence can be placed on results of this kind, that a method be devised which will take into account the internal strains existing in the metal at the time of testing.

F. W. HARRIS (written discussion).—In reply to Mr. Roush's discussion, in which he brings up the fact that the stresses in the inner portions of the wire are not necessarily the same before and after removing the outer layers by solution in acid, the author would state that this fact was not overlooked; it formed one of the reasons for making an exhaustive microscopic study of the internal structures, with a view to determining from the orientation of the crystals the major direction of these stresses. It would seem that they were largely tensile longitudinally, and compressive laterally but no attempt was made to measure their amount. Without a complete knowledge of these internal stresses it would be impossible, of course, to plot *absolute* curves of major stress variations by the method adopted. It is highly possible that the existence of heterogeneous stresses of the type illustrated by Mr. Roush may be the explanation of the different contours obtained in the author's curves.

How close the measured values approach the true ones is an open question, but accurate measurements of the latter by density, length, or volume changes would be expected to reveal some very interesting data in this connection.

Application of a High-vacuum Induction Furnace to the Study of Gases in Metals

BY P. H. BRACE* AND N. A. ZIEGLER,* EAST PITTSBURGH, PA.

(New York Meeting, February, 1928)

THE study of the relations between gases and metals is one of perennial interest to all who are connected with the production of high-grade metallurgical products. The data reported here are the outcome of work of which the object is to determine the effects of dissolved gases upon the properties of metals and to gain a more detailed knowledge of the reactions between gases and molten metals, particularly iron, under definitely controlled conditions.

We have attempted to reduce our margin of error by dealing with relatively large quantities of metal, from 4 to 13 lb. (2 to 6 kg.), and keeping the ratio of refractories to metal as small as practicable. The ingots produced are large enough to provide adequate material for making determinations of magnetic and other physical properties.

In choosing the bell-jar type of furnace we were influenced by the results of considerable experimentation along the same general line which indicated that, for the scale on which we were to work, it was important to have the furnace structure independent of the vacuum enclosure. The use of a bell-jar surrounding the entire furnace accomplishes this and also gives great freedom of observation during operation and ready accessibility for the replacements which are necessary after each run.

Our choice of analytical method was made in the light of the results secured by H. M. Ryder, who used a method similar in principle for the analysis of very small quantities of gas extracted from strips of metal heated electrically in high vacuum.

We have presented some selected preliminary experimental data as being illustrative of the quantity and nature of the gases which occur in iron of different origins, but do not urge any hypothesis at this time.

THE FURNACE

Our furnace may be described as "a high-frequency induction furnace of the bell-jar type." It is similar in a general way to that described by Cain and Peterson¹ though we have introduced certain refinements of

* Research Laboratory, Westinghouse Electric & Manufacturing Co.

¹ J. R. Cain and A. A. Peterson: A Laboratory High Frequency Vacuum Furnace. *Trans. Amer. Electrochem. Soc.* (1925) **48**, 139.

detail which make it possible to reach pressures as low as 0.0002 mm. mercury with 13 lb. (6 kg.) of molten iron in the furnace at a temperature above 1600° C. This has been accomplished by constructing the furnace entirely of metal and glass, providing vacuum connections of large bore—

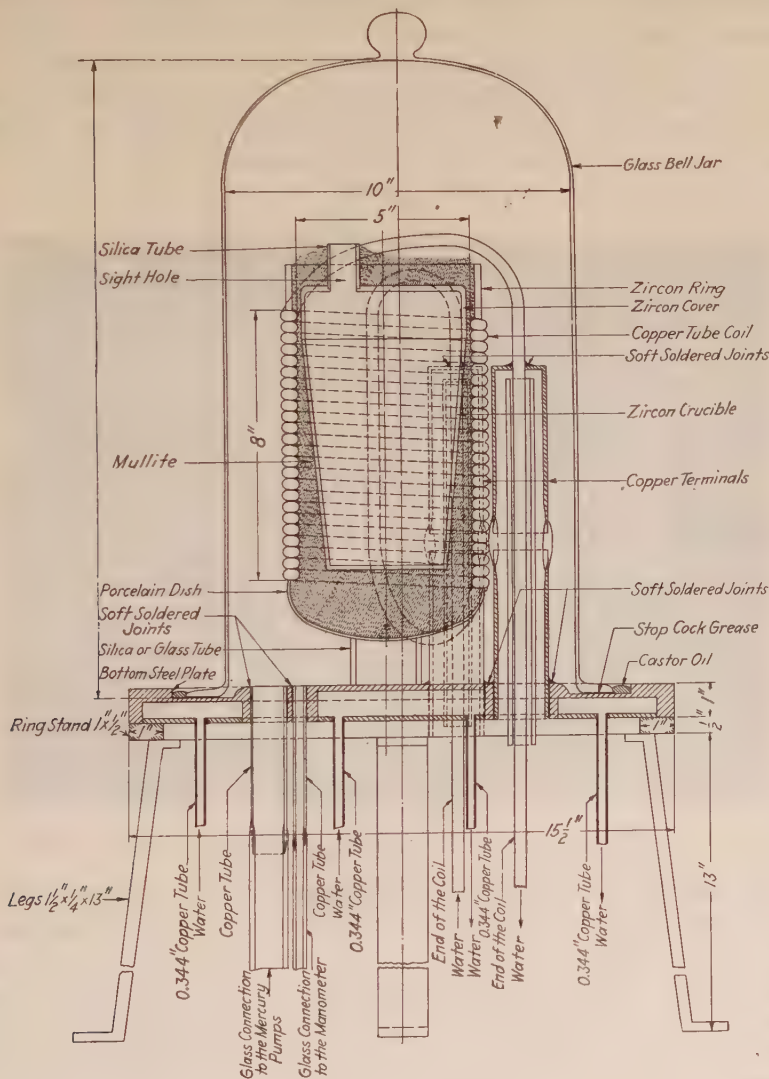


FIG. 1.—GENERAL VIEW OF BELL-JAR HIGH-VACUUM INDUCTION FURNACE.

1 in. (2.5 cm.)—and placing the high-vacuum mercury condensation pumps as close as possible to the furnace.

Power is supplied to the furnace at approximately 10,000 cycles per second from a Westinghouse motor-generator set driven by a direct-

current motor. Standard Westinghouse oil-insulated condensers are used in series with the furnace coil to compensate for its inductance and thus allow the generator to operate near unity power factor. Control of the power input to the furnace is secured by adjustment of the speed and excitation of the high-frequency generator. The use of a rotating generator allows power to be supplied to the generator in a continuous flow and not as a series of pulses, as is the case when a spark-gap oscillation generator is used. Thus the peak voltages across the inductor coil are much lower and few difficulties due to the occurrence of electrical discharges through the rarefied atmosphere in the furnace are encountered.

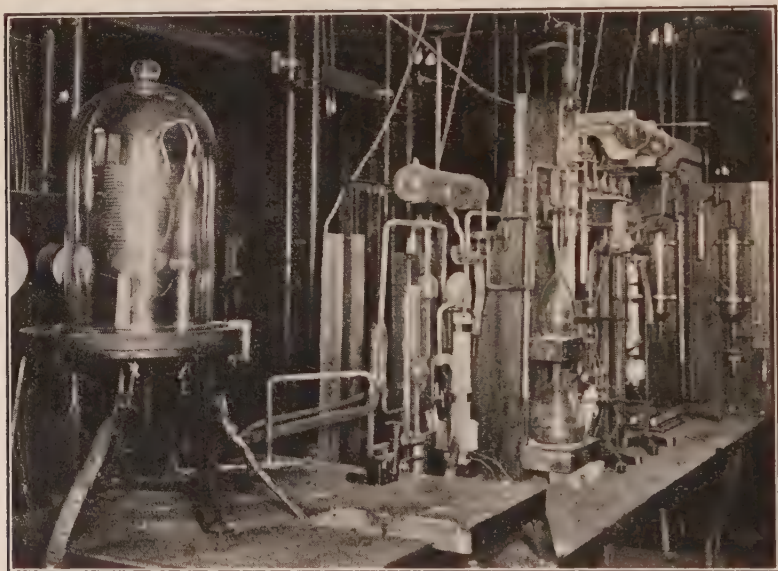


FIG. 2.—HIGH-VACUUM INDUCTION FURNACE AND GAS-ANALYSIS SYSTEM.

The construction of the furnace is shown in some detail by Fig. 1, and the general appearance by Fig. 2. The essential parts of the furnace are a water-cooled inductor coil mounted on a water-cooled steel baseplate by means of special insulated terminals, and covered by an ordinary glass bell-jar ground to fit the baseplate. The leads from the coil and all other connections for vacuum, manometers, etc., are brought through the baseplate by means of copper tubes soldered to the plate and sealed to the glass. The construction of these glass-copper seals is described below.

A typical inductor coil is made from copper tubing approximately 0.25 in. (0.635 cm.) I.D. by 0.35 in. (0.89 cm.) O.D. flattened to 0.27 in. (0.685 cm.) and wound on edge to form a helix having approximately 30 turns and an inside diameter of 5 in. (12.5 cm.). Several lengths of

copper tubing are required for such a coil and these are joined by machining the ends to corresponding internal and external tapers and uniting them with silver solder. Perfectly tight joints which withstand the

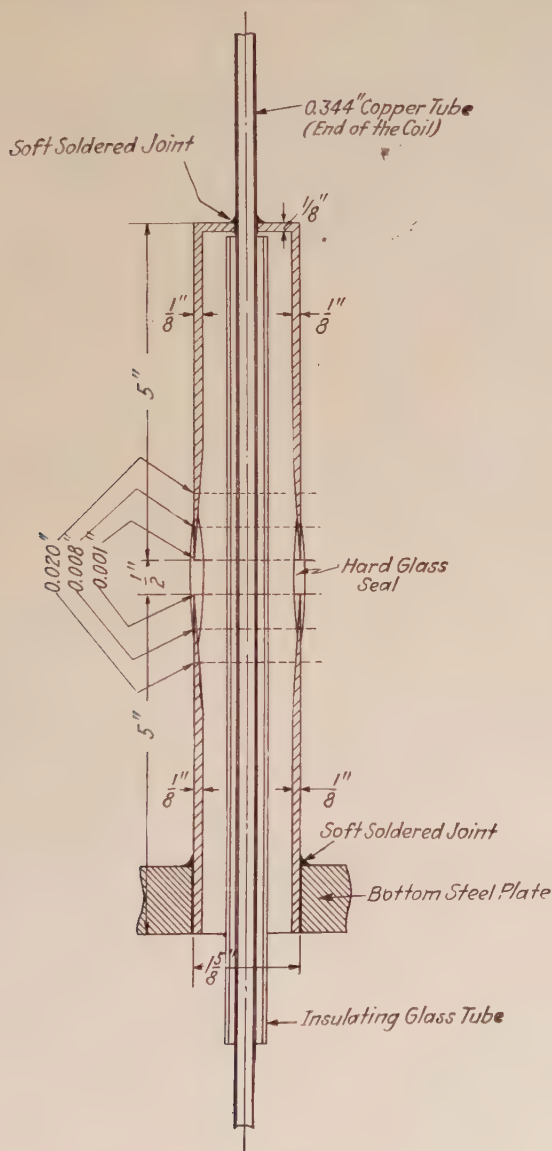


FIG. 3.—COPPER TERMINALS USED FOR BRINGING THE ENDS OF THE COIL FROM UNDER THE BELL-JAR

flattening and bending operations can easily be secured if the work is carefully done. Ordinary soft-soldered connections are unsatisfactory for these joints.

The bottom plate was machined from ordinary boiler-plate steel. The upper side has a shallow groove for the edge of the bell-jar, and recesses are machined on the under side which are covered to provide chambers for the cooling water. The baseplate is 15.5 in. (39.4 cm.) in diameter and 1 in. (2.5 cm.) thick.

The insulated coil-terminal by means of which the water and electrical power are brought through the baseplate and into the furnace is shown by Fig. 3. Two pieces of copper tubing are machined so that the wall thickness at one end of each increases uniformly from less than 0.001 in. (0.025 mm.) at the end to 0.008 in. (0.2 mm.) at 1 in. from the end, and uniformly from there to the full thickness of the tube wall.

Hard glass (G-702-P) is then fused inside and out over the thin edges thus formed to a distance of approximately 0.5 in. (1.2 cm.) from the end. The two tubes are then joined by fusing the glass together with the opposing edges of the copper approximately 0.5 in. (1.2 cm.) apart. In the same way copper connections are fastened to the glass tubing of the vacuum system and these copper connections are in turn soldered to the baseplate in order to provide reliable vacuum-tight connections between the glassware and the furnace.

The bell-jar is of the usual type purchasable from chemical supply houses and is 10 in. (25 cm.) in diameter by 19 in. (48 cm.) high inside. The lower edge is ground to an accurate fit with the steel baseplate, using emery and water as an abrasive and rotating the bell-jar to and fro in the groove in the baseplate with an occasional lifting and shift of its mean angular position. When this work has been properly done a very reliable seal can be obtained with a very small amount of stopcock grease and without applying pressure other than that due to the atmosphere. As an additional precaution, however, a small amount of castor oil is poured into the annular channel between the outside edge of the bell-jar and the side of the groove in the baseplate. With this set-up it is possible to reduce the pressure below 1×10^{-4} mm. mercury by means of two mercury-condensation pumps in series backed by a Trimount rotary oil pump.

The problem of refractories occupied a great deal of our effort at the outset of this work and while they are still the greatest source of difficulty and uncertainty we feel that this phase of the problem is reasonably well in hand and that no serious errors will arise from this source.

Fig. 4 shows the type of crucibles and covers that are now in general use. Type A is made from the purest obtainable zirconium silicate bonded with approximately 10 per cent. of refractory clay and fired at approximately 1500° C. Type B was at first made from a refractory porcelain similar to that used for pyrometer tubes. This ware was not sufficiently refractory, however, and a special ware was developed which is composed of a high percentage of pure fused alumina bonded with

aluminum silicate. These crucibles withstand temperatures well above the melting point of iron without appreciable softening and are also very satisfactory as regards the quantity of gas they release on heating.

Further precautions against evolution of "stray" gas during the operation of the furnace consist in keeping all the refractory parts in an electrically heated muffle furnace at a temperature of approximately 1000°C . for several hours prior to use, and assembling them in the furnace while still hot in order to drive off as much gas as possible before use and to afford as little chance as possible for re-absorption during assembly.

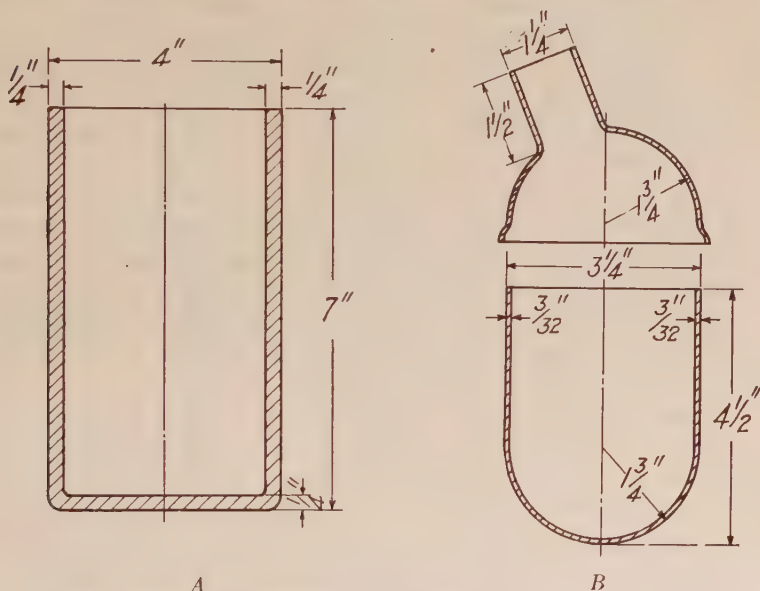


FIG. 4.—CRUCIBLES. A, ZIRCON; B, PORCELAIN.

The interior of the bell-jar is carefully cleaned after each run to remove the black deposits of vaporized metal which condense during operation of the furnace. In some cases a brilliant mirror condenses on the wall of the bell-jar opposite the sight tube, and the accumulation is always greatest at that point. The metal parts within the furnace, and particularly the coil, are cleaned with abrasives at frequent intervals to remove the finely divided deposits which accumulate and adsorb appreciable quantities of gas and moisture, which would be released under operating conditions to an unknown and variable extent.

OPERATION OF THE FURNACE

The arrangement of the coil and the refractories when set up for melting is shown by Fig. 1. A short length of silica or glass tubing, resting on the baseplate, supports a porcelain evaporating dish which closes

the lower end of the coil and supports the granular fused aluminum oxide (R.R. alundum, 20 mesh, from the Norton Co.) which is used as thermal insulation and support for the crucible. The granular alumina is poured into the dish to the level desired for the bottom of the crucible. The crucible is set in concentric with the coil and covered, and alundum is poured in to fill the space between the crucible and coil to the top edge of the crucible. The heat losses during operation are thus greatly reduced and no harm results from cracking of the crucible because the granular material forms an effectual barrier for the molten metal.

The charge is next packed as compactly as possible into the crucible, avoiding jamming, however, so that its thermal expansion will not cause breakage of the latter. The crucible cover is put in place and alundum poured in to cover it to a depth of approximately 1 in. (2.5 cm.). The turns of the coil are then pried apart slightly, to allow a few granules to run between them here and there and thus insulate each turn from the next. Loose particles which have fallen on to the baseplate are brushed off, the ground surface is wiped clean and the bell-jar, with its ground edge coated with grease, is put in place. The furnace is partly evacuated and meanwhile the bell-jar is moved slightly to and fro in order to work the grease into a thin film and eliminate any air pockets. The external annular groove between the bell-jar and baseplate is then filled with castor oil and all is in readiness for final evacuation.

The furnace is exhausted to approximately 2 cm. mercury by direct connection to the house vacuum and from there on by means of the mercury and oil pumps. Meanwhile steam is passed through the inductor coil to heat it above normal operating temperature and thus to remove from the coil and charge surface gases and moisture, which might otherwise be liberated during operation of the furnace. The pumps are allowed to operate with steam passing through the coil until the McLeod gage shows a pressure less than 0.001 mm. mercury. This requires from 2 to 4 hr., depending largely on the condition of the charge. When this is in small pieces, making the surface large, more time is required to eliminate these surface gases. Noticeable amounts of gas are also liberated from the bell-jar and coil in the early stages of evacuation.

When a satisfactory vacuum has been obtained the flow of steam through the coil is replaced by water, circulation of water through the bottom plate is established and the melting operation may then proceed. The furnace is now connected to the power supply and heating proceeds at a rate dependent on the circumstances and the behavior of the charge. Gas is evolved from the charge as soon as heating commences and the pressure under the bell-jar rises in consequence. If heating is carried out too rapidly, the pressure will rise to such a point that electrical discharges occur through the gas within the bell-jar because of the fact

that the potential across the coil may reach a few hundred volts. A blue glow, which is harmless, is frequently present but when this gives way to sparking the power input must be reduced in order to forestall arcing which might cause damage to the furnace or electrical equipment.

A condensed log of a typical furnace run is given in Table 1. The charge consisted of 3.48 lb. (1.575 kg.) of cleaned electrolytic iron in the form of pieces approximately 1 in. (2.5 cm.) square and 0.125 in. (0.3 cm.) thick, stacked flatwise in the crucible.

TABLE 1.—*Condensed Log of a Typical Furnace Run*

Run 135. Charge: Electrolytic Iron, 1575 Gm. (3.48 Lb.)			
TIME	CURRENT, AMPERES	PRESSURE, MM. HG.	
1:50	100	0.0001	Charge temp. approx. 700° C.
1:55	150	0.06	
2:00	158	0.04	
2:05	170	0.025	
2:10	174	0.088	
2:15	174	0.070	
2:20	176	0.140	Melting commenced.
2:25	178	0.100	
2:30	184	0.120	
2:40	170	0.080	Charge molten.
2:45	170	0.035	
2:50	174	0.035	
2:55	172	0.030	
3:00	174	0.025	
3:05	174	0.020	
3:10	174	0.018	
3:15	174	0.015	
3:20	174	0.013	
3:25	174	0.010	
3:30	174	0.005	
3:35	174	0.003	
3:40	174	0.001	
3:45	174	0.0008	
3:50	174	0.0003	
3:55	174	0.0002	
4:00	174	0.0002	
4:05	174	0.0002	
4:10	174	0.0002	
4:15	174	0.0002	
4:20	174	0.0002	
4:25	174	0.0001	
4:30	0	0.0001	Power off.

A complete diagram of the furnace and associated system is shown by Fig. 5. A mercury manometer is connected directly to the furnace chamber and a McLeod gage is connected to the exhaust tube between the furnace and the vacuum pumps. A two-way stopcock connected to

the manometer tube enables communication to be established between the furnace chamber and either one of two outlets. In mid-position both passages are closed. This provides means for rapidly removing the major portion of the air from the furnace when starting a run and also allows for the admission of desired gases during the operation of the furnace. A ground plug with two tungsten leads sealed through is provided to allow for the installation of a thermocouple within the bell-jar and to bring its leads outside for connection to a pyrometer.

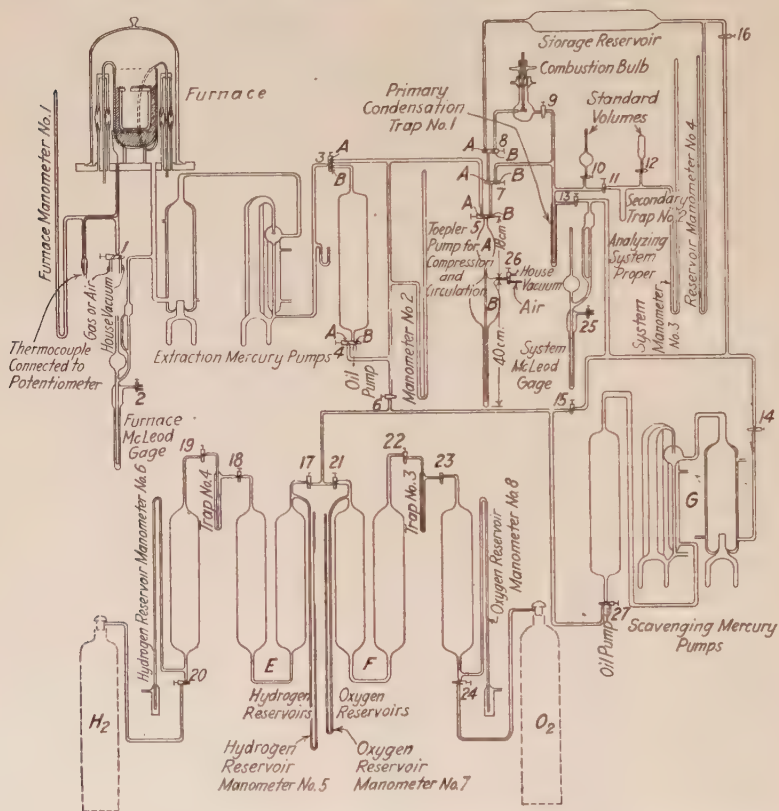


FIG. 5.—APPARATUS FOR ANALYSIS OF GASES EXTRACTED FROM MOLTEN METALS

ANALYTICAL SYSTEM AND PROCEDURE

Reference has already been made to Fig. 5 in connection with the portions of the vacuum system immediately associated with the furnace as distinguished from the analysis system proper. We will now describe the analysis system and its manipulation, with reference again to Fig. 5.

Toepler Pump.—This is in effect a pneumatically driven pump with a mercury "piston" which sweeps the volume of the upper bulb, A, in

response to changes of air-pressure applied to the mercury in the bulb *B*. The gases discharged from the second-stage extraction pump are admitted to the upper bulb of the Toepler pump by way of stopcocks 3*A* and 5*A*. Atmospheric pressure is applied to the mercury in the lower bulb and stopcock 5 turned to position *B* and the gases forced into the storage reservoir through stopcocks 7*A* and 8*A*. The Toepler pump is

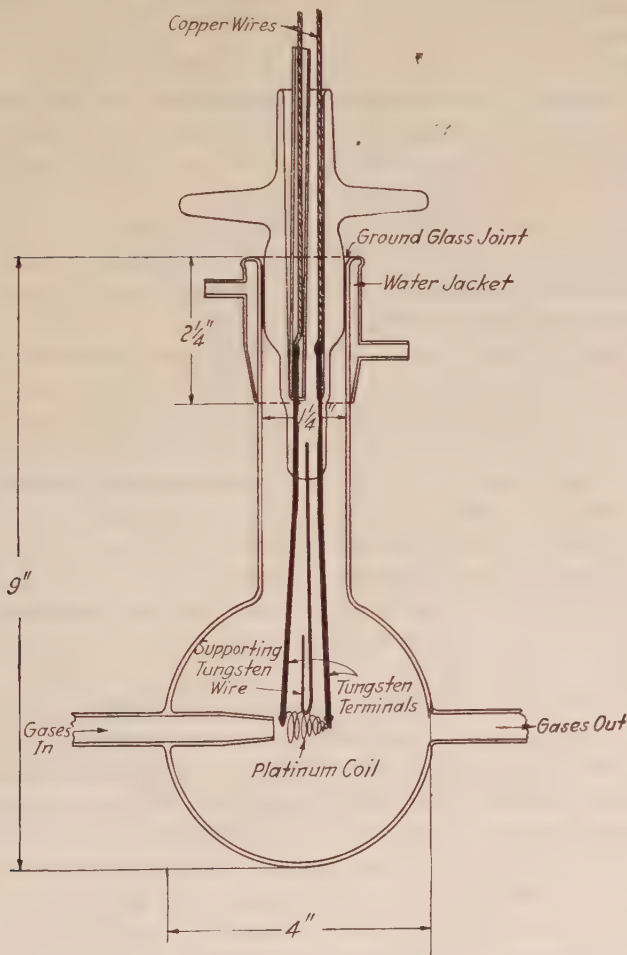


FIG. 6.—COMBUSTION BULB.

also used to withdraw gases from the storage reservoir, to circulate them through the absorption trap and combustion bulb, and in general for handling them during analysis.

Combustion Bulb.—The location of the combustion bulb in the analytical system is shown by Fig. 5 and the details of its construction by Fig. 6. It consists of an approximately spherical glass bulb² provided with three

radial side tubes 90° apart and in the same plane. The opposite tubes serve as inlet and outlet respectively. A conical helix of platinum wire is supported opposite the inlet tube by an assembly which is introduced through the intermediate side tube and is mounted on a plug which fits on a ground seat in the outer end of the side tube. This joint is made tight with stopcock grease, and it was necessary to water-jacket it to avoid leakage due to softening of the stopcock grease by heat from the filament.

Primary Condensation Trap.—The primary condensation trap (No. 1, Fig. 5) consists of an elongated bulb into which is sealed a concentric tube reaching nearly to the bottom, with outlets from the central tube and external bulb. The annular space between the bulb and the tube is loosely packed with glass wool. Gases to be condensed are passed downward through the central tube and up through the annular space where the glass wool assists in retaining any condensate which may have been precipitated as mist or snow. Arrangements are made so that containers with liquid air, CO_2 snow or water may be brought up from below to immerse the trap and thus bring it to a desired temperature.

Expansion and Measuring System.—This portion of the system includes a secondary condensation trap (No. 2, Fig. 5), two "standard volume" bulbs of which the cubical capacities are accurately known, and a system manometer (No. 3). The manometer indications, together with knowledge of the connected volume, are used to calculate the amounts of gas in the measuring system. A McLeod gage ("System McLeod Gage," Fig. 5) is connected to the analysis system to enable the measurement of low pressures and thus determine when the latter has been cleared of gas prior to the introduction of a fresh portion to be analyzed.

After a given gas has been condensed in the primary trap, the Toepler pump is operated to pump residual gas into the primary storage reservoir until the pressure in the primary trap and expansion system is 0.001 mm. mercury or less. The primary trap and the expansion system are then isolated and the coolant is removed from the primary trap and placed about the secondary trap, thus causing the condensed gases to evaporate from the former and condense in the latter. When the transfer is complete the expansion system is isolated, the coolant is removed from the secondary trap and the condensate allowed to expand, first into the known volume including the trap and system manometer No. 3 and limited by stopcocks 11 and 12 and, in some cases to be discussed below, into successively larger known volumes made available by opening stopcocks 12, 11, and 10, in the order named. The quantity of gas in the expansion and measuring system is known from the readings of the system manometer No. 3 and the volume of the region in which expansion has taken place.

Reagent Reservoirs.—Two sets of reservoirs (*E* and *F*, Fig. 5) are provided to store purified gases, usually oxygen and hydrogen for use in connection with the analytical procedure. The volumes of these reservoirs are known and they are provided with manometers so that the quantity of gas available as well as the amounts withdrawn may be determined quantitatively.

Scavenging Pumps.—Two mercury pumps (*G*, Fig. 5) in series with an oil pump are provided to remove gases from the analytical system, and if necessary, from all other parts of the system. Gas fractions which have been isolated and measured are thus removed from the analytical system, to make way for subsequent operations.

ANALYTICAL PROCEDURE

Let us assume that a furnace run has been carried to completion; *i.e.*, to such a point that the rate of gas evolution from the furnace has become inappreciable as judged by the fact that the pressure indicated by the manometer attached to the storage reservoir has remained constant over a considerable period of time during which the Toepler pump has been operated systematically to force any gas received from the furnace into the storage reservoir.

The mixture of gases to be expected from a normal furnace run will contain H_2 , N_2 , O_2 , CO , CO_2 and H_2O . We have not attempted to analyze for SO_2 as yet. We will assume that such a mixture is to be analyzed, that it is all in the storage reservoir and that all other parts of the analytical system beyond stopcocks 3*B* and 4*A* have been pumped well below 0.001 mm. by means of the scavenging pumps.

The first step is to remove the H_2O by circulating the contents of the storage reservoir through the primary condensation trap while the latter is immersed in CO_2 snow, by way of the circuit through stopcocks 8*A*, 7*A*, 5*B*, 5*B*, 7*B*, 13, 16, 8*A*. When removal of H_2O vapor is complete as shown by constancy of the indication of the storage manometer, stopcock 16 is closed and the residual gases pumped into the storage reservoir by means of the Toepler pump. Pumping is continued until the system McLeod gage shows a pressure below 0.001 mm. mercury. Under these conditions the amount of CO_2 condensed with the water amounts to approximately 0.4 per cent. of the latter.

Stopcocks 7, 9, 10, 12 and 13 are now closed, boiling water is placed about the primary trap and the CO_2 snow is transferred to the secondary trap, causing the H_2O to evaporate from the primary trap and condense in the secondary trap. The transfer is complete in approximately half an hour and then stopcock 11 is closed, 12 is opened, and boiling water is placed about the secondary trap to cause the condensed water to evaporate. Evaporation will continue until all the water has vaporized

or until the pressure in the volume available for expansion has risen to approximately 20 mm. mercury, corresponding to the vapor tension of water at ordinary temperatures.

The system manometer (No. 3) is then read, the volume available for expansion increased by opening stopcock 11 and another manometer reading taken when the pressure has become constant. If liquid water still remains, this reading will differ little if any from the first, and additional increases in available volume must be made by opening stopcocks 13 and 10 successively until the manometer shows a permanently lowered reading, indicating that all the water is in the form of vapor. From the succession of manometer readings and knowledge of the volumes of the various portions of the system, a series of values for the amount of water vapor are calculated, and the highest is taken as correct.

The next step is to reject the water vapor by opening stopcock 14, which connects the analysis system to the scavenging pumps; this communication is maintained until the system McLeod gage shows a pressure less than 0.001 mm. mercury.

Next, CO_2 is isolated from the residual mixture, which has meanwhile been retained in the storage reservoir, by following a procedure which differs from that just described for water only in the following particulars: that liquid air instead of CO_2 snow is used for cooling the traps, and that because of the high vapor tension of CO_2 at ordinary temperatures, its quantity can be determined from the first reading of manometer No. 3 and the successive increases in available expansion volume are unnecessary except as a means of guarding against possible errors of observation or calculation. The difference between the pressures in the storage reservoir before and after condensation of the CO_2 furnishes an additional check on the results obtained from the direct measurement described.

The gaseous residue now remaining in storage contains H_2 , N_2 , O_2 and CO , and the next step is to cause combination of the combustible gases with the oxygen present. The filament of the combustion bulb is brought to a bright red heat and the Toepler pump is operated to circulate the gases from the storage reservoir through the combustion bulb and primary trap by way of the circuit through stopcocks 8A, 7A, 5B, 7A, 8B, 9, 13, 16. Meanwhile, the primary trap is cooled with CO_2 snow and any H_2O which has been produced by reaction in the combustion bulb is thus trapped, measured and rejected as described above. The remaining gas is again circulated with liquid air at the trap and any CO_2 produced is determined as before.

We now have in the storage reservoir a gaseous mixture of N_2 with either O_2 or H_2 and CO and have no means of knowing with certainty whether it is the oxygen or the combustible gases that are present. At this point we make use of one or the other of the gases from the reagent reservoirs, and the choice is a matter of judgment. In general, if water

and considerable quantities of CO_2 have been produced in the combustion bulb, it will be expected that, except for nitrogen, the residue will be oxygen rather than hydrogen or CO. Assume that oxygen remains, that the residual gas mixture has been transferred by the Toepler pump to the storage reservoir, and that all other parts of the storage system have been freed from gas by means of the scavenging pumps.

A volume of hydrogen equal to twice that of the gas mixture already in the storage reservoir is introduced into the latter by means of the Toepler pump by way of stopcocks 17, 6, 5A, 5B, 7A, 8A. This will triple the pressure indicated by the reservoir manometer (No. 4). This quantity of hydrogen will be sufficient to combine with all the oxygen present in the extreme case of there being but inappreciable quantities of N_2 present, and no CO. Stopcocks 16 and 8A are now closed, the system outside the storage reservoir is exhausted by means of the scavenging pumps; the gas mixture in the storage reservoir is circulated through the combustion bulb and primary trap (No. 1) as before, and the products of reaction estimated and rejected, using CO_2 snow as coolant for the traps.

If no water has been formed, it must be assumed that nitrogen only, or else a mixture of nitrogen with hydrogen, CO, or both, was present before the reagent hydrogen was added. The water resulting from the reaction is then a measure of the oxygen in the residue prior to the introduction of the reagent hydrogen, H_2 and CO were presumably absent and the final residue after subtracting the uncombined hydrogen is nitrogen or other inert gas. In either case, a final check is made by returning the last uncondensed residue to the storage reservoir, adding an equal volume of reagent oxygen by following a procedure similar to that used in the case of the reagent hydrogen, carrying out combustion as previously, and measuring the reaction products condensed by CO_2 snow and liquid air respectively.

If only water is formed, it indicates that our original surmise as to the nature of the residue over and above nitrogen was correct. Otherwise both water and CO_2 will be formed and from our knowledge of these quantities, those of the added reagents, that of the residue just before adding the reagents, and that of the final residue now in hand, we can calculate the composition of the residue which was last in the storage tank before any reagent gases were added, the composition of the final residue, and hence the total composition of the mixture with which we started.

DETERMINATION OF GASES IN METALS

The determination of the gases evolved from a given sample of metal involves not only the analysis of the total quantity of gas collected during the furnace run but also a knowledge of the gases liberated from

other parts of the furnace and in particular from the crucible and other refractories used to contain the molten metal. Our practice, as has already been noted, is to pre-treat all the refractory parts at a temperature near 1000° C. for several hours before use and to assemble them while hot and proceed with evacuation immediately in order that there may be as little opportunity as possible for re-absorption of moisture and other gases from the air. It was recognized that the above treatment did not remove all absorbed gases, and that at the temperatures which we expected to reach when dealing with iron and iron alloys, serious errors might be caused by further evolution of gases unknown as to nature and amount.

In order to reduce this source of error to a practicable minimum, several runs were made for which the furnace was set up in the usual way and in which the charge consisted of a cylinder of sheet molybdenum which was fitted as closely as possible to the walls of the crucible. After a preliminary run to degasify the molybdenum, another set-up was made to determine the gases released from the refractories, assuming that the amount coming from the small amount of degasified molybdenum would be negligible as compared to that from the fresh refractories.

A second method, and one which was used in connection with our work on iron, was carried out as follows. A set-up was made in the usual way, using preheated refractories and cleaned iron. The operation of the furnace was carried out as usual, although the heating period was somewhat prolonged in order to insure complete degasification of the iron. The melt was allowed to solidify in the crucible and the extraction pumps were kept in operation continuously until the metal was cold. The ingot was removed, cleaned, and used as the charge in a second run with a new set of refractories. The gases evolved in the second run were presumed to come from the refractories, inasmuch as great care had been taken to complete the degasification of the iron. Four such "blank" determinations were made, of which the results are shown by Table 2.

TABLE 2.—*Tests of New Refractories to Determine Gases Evolved*

Run No.	Material of Charge	Crucible Material	Gases Evolved, Cubic Centimeters						
			H ₂ O	CO ₂	CO	O ₂	H ₂	N ₂	Total
114	Electrolytic iron	Zircon	7.1	11.7	35.5		59.3	8.1	121.7
116	Electrolytic iron	Zircon	11.3	8.9	27.7		44.3	10.5	102.7
142	"Armco ingot iron"	Alumina-aluminum silicate	10.9	7.5	24.6	0.4	52.0	5.8	101.2
144	"Armco ingot iron"	Alumina-aluminum silicate	8.5	6.0	24.9	1.0	52.4	4.7	97.5
		Averages.....	9.2	8.5	28.2	0.35	52.0	7.3	105.7

These data are fairly consistent. The averages from these four runs were used as the corrections to be applied to the results of runs made to determine the gas content of metal samples when operating with similar refractory conditions. The correction, which usually totaled approximately 10 per cent., was made by subtracting the averages from the corresponding totals found for the gases from the melt being considered. In the data presented below only the corrected totals are given.

Gases from Iron

The data shown by Table 3 were obtained by melting a 1200-gm. charge of cleaned electrolytic iron deposited from a mixed chloride-sulfate bath. The chemical analysis was as follows: carbon, 0.032 per cent.; silicon, 0.005; sulfur, 0.004; phosphorus, 0.004; copper, 0.018; lead, nil; manganese, nil; nickel, nil.

TABLE 3.—*Gases from Electrolytic Iron*

Gas	Cubic Centimeters Evolved	Per Cent. of Volume of Charge	Per Cent. of Weight of Charge	Per Cent. of Total Volume Evolved	Per Cent. of Total Weight Evolved
H ₂ O.....	10.8	6.9	0.0007	2.7	1.7
CO ₂	66.9	42.9	0.0103	16.8	26.0
CO.....	287.9	184.5	0.0295	72.2	70.4
O ₂	5.3	3.4	0.0006	1.3	1.5
H ₂	27.8	17.8	0.0001	7.0	0.4
N ₂	Nil	Nil	Nil	Nil	Nil
Totals.....	398.7	255.5	0.0424	100.0	100.0

The results of a similar run on Armco ingot iron are given by Table 4. The material was in the form of commercial hot-rolled plates approximately 0.25 in. (0.63 cm.) thick. Prior to melting, it was cleaned by grinding off all scale on a dry carborundum wheel and sheared cold to convenient sizes for charging. Chemical analysis gave the following results: carbon, 0.0123 per cent.; manganese, 0.025; sulfur, 0.019; phosphorus, 0.005; silicon, traces; chromium, traces.

If the data of Tables 3 and 4 be compared, some interesting observations can be made. The electrolytic iron evolved a certain amount of water, while none was recovered from the Armco iron. This is in line with the fact that electrolytically deposited metals often contain inclusions of electrolyte. On the other hand, appreciable quantities of nitrogen were obtained from the Armco iron sample and none from the electrolytic iron. The total volume and the total weight of gas evolved

from the electrolytic iron are approximately 25 per cent. greater than from the Armco ingot iron, and this is also in line with expectations based on the known characteristics of the two materials.

TABLE 4.—*Gases from Armco Iron*

Gas	Cubic Centimeters Evolved	Per Cent. of Volume of Charge	Per Cent. of Weight of Charge	Per Cent. of Total Volume Evolved	Per Cent. of Total Weight Evolved
H ₂ O.....	nil	nil	nil	nil	nil
CO ₂	72.5	27.1	0.0067	14.4	20.8
CO.....	389.6	145.5	0.0236	77.1	73.3
O ₂	2.8	1.1	0.0002	0.6	0.6
H ₂	10.3	3.9	0.00005	2.1	0.2
N ₂	28.0	11.0	0.00164	5.8	5.1
Totals.....	503.0	188.6	0.0322	100.0	100.0

Samples of electrolytic iron and of Armco ingot iron were treated as follows:

1. Melted and degasified in usual manner.
2. Maintained molten for 2.5 hr. under purified hydrogen at one atmosphere and flowing at a rate of 500 c.c. per min.
3. Cooled in hydrogen flow.
4. The hydrogen-treated ingot placed in new set-up, remelted and the evolved gases analyzed.

The data obtained from these two sets of runs have been condensed to form Table 5, which shows the quantities of the elements O₂, H₂, N₂, and C evolved at each stage of the procedure in terms of the weights and volumes of the charges used. Study of these data will show some interesting facts:

(a) The total weight of elements removed from the electrolytic iron was approximately 70 per cent. greater than from the Armco ingot iron and their volume was 65 per cent. greater.

(b) Nitrogen was evolved from the Armco ingot iron but not from the electrolytic iron.

(c) Considerable quantities of gas were recovered from the electrolytic iron by the second degasification while the Armco ingot iron yielded no measurable amounts. This fact is of particular interest but cannot be definitely explained at this time.

Another fact of considerable interest has been noted; namely, that for both electrolytic and Armco ingot iron the weights of carbon and oxygen eliminated as gas during vacuum degasification bear an approximately constant ratio to one another and to the total quantity of gas eliminated. This condition has been observed with a number of heats

and for widely different initial conditions. Typical data are shown by Table 6.

TABLE 5.—*Elements Evolved as Gas from Iron by Degasification, Hydrogen Treatment and Repeated Degasification*

Material	Treatment	Elements Evolved									
		O ₂		H ₂		N ₂		C		Total	
		Per Cent. of Charge		Per Cent. of Charge		Per Cent. of Charge		Per Cent. of Charge		Per Cent. of Charge	
		Weight	Volume	Weight	Volume	Weight	Volume	Weight	Volume	Weight	Volume
Electrolytic iron	Vacuum degasification.....	0.0263	142.1	0.00024	24.7			0.0159			
	Hydrogen treatment.....	0.0651	349.8								
	Vacuum degasification.....	0.0352	180.1	0.00056	70.2			0.0229			
	Total.....	0.1267	672.0	0.00080	94.9			0.0388		0.1663	766.9
Armco ingot iron	Vacuum degasification.....	0.0186	101.0	0.00005	3.9	0.00164	11.0	0.01194			
	Hydrogen treatment.....	0.0642	346.0								
	Vacuum degasification.....										
	Total.....	0.0827	447.0	0.00005	3.9	0.00164	11.0	0.01194		0.0964	461.9

TABLE 6.—*Relation between Oxygen and Carbon Removed as Gas from Electrolytic and Armco Ingot Iron*

Melt No.	Initial Condition of Charge	Weight Percentage of Total Gas		Ratio C/O ₂
		As Carbon	As Oxygen	
140	Electro. iron cleaned previously.....	37.3	62.1	0.60
121	Electro. iron oxidized while molten with oxygen	37.5	60.5	0.62
136	Previously hydrogen-treated while molten....	38.9	59.8	0.67
139	Previously hydrogen-treated while molten....	38.4	59.1	0.65
141	As received, cleaned.....	37.1	57.7	0.65
143	As received, cleaned.....	37.5	56.7	0.66

These results are quite surprising when it is remembered that both the total quantity and the relative amounts of the components of the gas mixtures differed widely.

THEORY

Very few results have been published on the solubility of gases in iron as related to temperature. For that reason the theory of the physical and chemical reactions going on in molten iron is not well

established and the details of the complicated reactions are very obscure. The complexity of the situation will be realized when we consider the number of physical and chemical possibilities, of which the following are only a few:

1. Reaction of gases with iron.
2. Reaction of gases with iron oxide.
3. Solution of gases in iron.
4. Solution of gas-iron compounds.
5. Temperature effects on equilibrium of chemical reactions.
6. Temperature effects on solubilities.

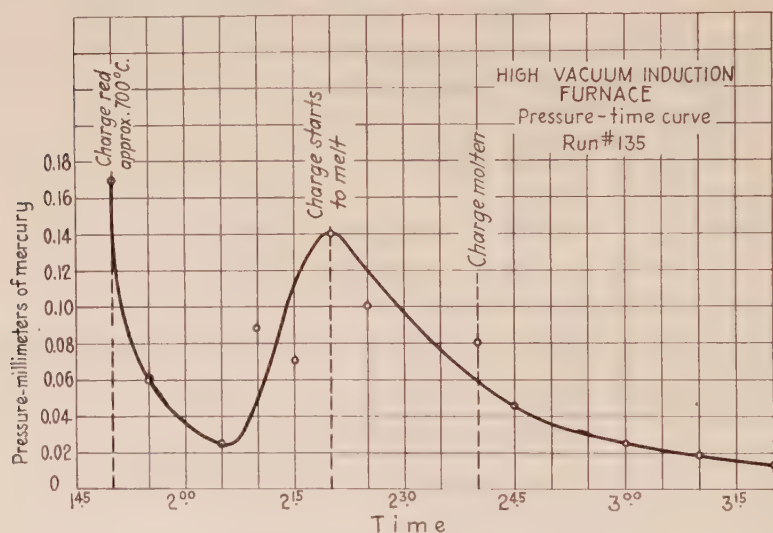


FIG. 7.—PRESSURE-TIME CURVE, RUN NO. 135.

This is aside from the effects of metallic elements other than iron, which would still further complicate matters. Of the many who have worked in the solubility of gases in various metals, Sieverts of Germany² has done valuable work. Much credit is also due Iwasé, of Japan,³ who has obtained some very interesting data on the solution of gases by various metals as related to temperature. His work with iron showed that its solvent power for H_2 and N_2 increased linearly with the temperature and that the slopes of the solubility temperature curves changed abruptly at $910^\circ C.$, corresponding to the alpha-gamma transformation

² A. Sieverts: Zur Kenntnis der Okklusion und Diffusion von Gasen durch Metalle. *Zeitschr. phys. Chem.* (1907) **60**, 129.

³ K. Iwasé: Equilibrium between Iron, Carbon and Oxygen. *Sci. Repts. Tohoku Imp. Univ.* [1] (1926) **15**, 511.

Occlusion of Gases by Metals and Alloys in Liquid and Solid States. *Ibid.*, 531.

where the atomic arrangement changes from body-centered cubic to face-centered cubic.

If we plot the time-pressure curve (Fig. 7) for our furnace during a run in which the temperature has been increased as uniformly as possible, we find that the pressure rises to a sharp maximum just before the charge begins to melt, indicating that the rate of gas evolution has increased very markedly. This phenomenon is interesting when considered in the light of Iwasé's data, which show an abrupt increase in the solubility of gases coincident with the change of atomic arrangement from body-centered cubic to face-centered cubic, and it is not unreasonable to suppose that a reversion to a body-centered arrangement would result in decreased solvent power and cause the rejection of gases from solid solution coincident with the gamma-delta transformation which occurs at 1410°C. , a temperature which corresponds approximately to the upturn of the pressure-time curve noted above. At this temperature diffusion of gas through the metal could take place relatively easily and gases rejected on account of change in the solvent power of the metal would be promptly released. The approach to the maximum pressure on our curve covers some little time interval, but this would be expected from the fact that the charge is not quite uniformly heated, hence some portions will pass through the transformation range earlier than others.

The foregoing explanation of the high rate of gas evolution from iron, which we have found to occur just before melting, is not put forward as an established fact but as an interesting possibility, and more critical experimentation must be done before definite statements are made.

CONCLUSION

1. A high-frequency vacuum furnace has been constructed capable of melting 13 lb. (6 kg.) of iron and maintaining it at temperatures above 1600°C. under a pressure less than 0.0005 mm. of mercury.

2. An analysis system has been constructed for analyzing quantitatively the gases from the furnace with respect to H_2 , N_2 , O_2 , CO , CO_2 and H_2O . The separation of the mixtures into their components is accomplished by selective condensation and combustion and volumetric measurements for estimating quantities.

3. The technique of furnace operation and gas analysis has been described.

4. Experimental data showing the results obtained from the analysis of gases from iron are presented and certain consistencies are pointed out. Peculiarities of the relation between the rate of gas evolution from iron as related to temperature are tentatively explained on the basis of the changes in its atomic structure, which occur at approximately 900°C. and 1410°C.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to the Westinghouse Electric & Manufacturing Co., in whose research laboratory this work was done, for permission to publish these results.

The Vesuvius Crucible Co., of Swissvale, Pa., and the McDanel Refractory Porcelain Co., of Beaver Falls, Pa., gave valuable assistance in connection with the development of special crucibles.

Thanks are due H. M. Kraner of the research laboratory of the Westinghouse Electric & Manufacturing Co., for helpful suggestions in connection with refractories problems and great credit is due C. Kirwer, also of the research department, for the excellence of his work on the glassware of the analytical system.

DISCUSSION

L. JORDAN and H. C. VACHER, Washington, D. C. (written discussion).—Our experience at the Bureau of Standards for the past several years in the development and application of vacuum fusion methods for determining gases in metals makes this contribution by Messrs. Brace and Ziegler of very great interest. We can well appreciate their statement that the refractories "were the greatest source of difficulty and uncertainty."

In our first attempts to work out a satisfactory vacuum fusion method for oxygen and hydrogen⁴ we fused iron and steel samples in refractory oxide crucibles. We anticipated difficulty in making oxygen determinations with such a method of melting from the probable reactions between the refractory oxides of the crucible and the carbon or iron carbide in solution in the metal sample, with the resulting decarburization of the melt and the evolution of oxygen (as carbon monoxide) whose source was the crucible rather than the metal sample.

We found that decarburization of a 0.25 per cent. carbon steel did take place when fused in vacuum in the high-frequency induction furnace in crucibles of magnesite, alumina, alumina bonded with silica, or alumina bonded with zirconium silicate. A crucible of zirconium oxide bonded with alumina, and fired in such a manner as probably to have a surface largely of carbide, was the most promising of those tested, in that the 0.25 per cent. carbon steel held molten for approximately 3 hr. in this refractory lost only 0.02 per cent. carbon. Even this crucible was unsatisfactory with higher carbon steels.

Brace and Ziegler, of course, have worked with irons of still lower carbon content, cathode electrolytic iron containing 0.032 per cent. carbon and Armco ingot iron containing 0.012 per cent. carbon. We believe, however, that even in these cases they have actually extracted and determined the CO and CO₂ resulting from reaction between the carbon of the iron samples and the oxides of the containing crucibles. This is indicated by the data they give in Table 5 on the carbon evolved in gases, expressed as per cent. of the iron sample. It will be noted in this table that, in the case of the electrolytic iron, the first vacuum degasification resulted in the evolution in the gases of 0.016 per cent. carbon. After the intervening hydrogen treatment, the

⁴L. Jordan and J. R. Eckman: Gases in Metals. II. The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum. Bur. of Stds. *Sci. Paper* 514 (1925).

second vacuum degasification yielded even more oxygen than did the first vacuum fusion; the carbon content of these gases was 0.023 per cent. and this amount, added to the carbon evolved in the first fusion of the sample, gave 0.039 per cent. total evolved carbon, which is all the carbon present in the original electrolytic iron sample. The reduction of the crucible refractory and the evolution of oxygen therefore continued as long as carbon remained in the iron.

The reason for the Armco iron sample failing to yield any measurable amounts of gas in the second vacuum degasification (following the hydrogen treatment) would appear to be that the first vacuum melting of this sample evolved 0.012 per cent. carbon and the original carbon of the sample was precisely that value, 0.012 per cent. There remained, therefore, no carbon to bring about reduction of the crucible refractories in the second vacuum fusion. The reduction of the crucible refractory and the evolution of oxygen therefore ceased as soon as carbon was eliminated from the iron sample. More oxygen may still remain in the sample.

In the procedure used for the determination of "blanks" (Table 2) it should also be assumed that decarburization of the iron samples took place in the initial vacuum degasification. This decarburization may well have been quite complete, even in the case of the electrolytic iron, since it is stated that "the (initial) heating period was somewhat prolonged in order to insure complete degasification of the iron." The amounts of gas evolved by the remelting of these carbon-free charges in new refractories may represent the gases adsorbed by the refractories but cannot correctly represent the gases liberated from the crucible by reaction with the carbon of the melt in the actual determinations with fresh samples.

Further, it seems doubtful, at least in the absence of any mention of blanks for the "hydrogen treatment," if all the oxygen evolved from the electrolytic and Armco irons by hydrogen treatment (Table 5) can be regarded as gas present in the original iron samples. It may in part represent reduction of crucible oxides. It has been our experience in melting pure metals at temperatures of 1500° to 2000° C. that such oxides as magnesia and zirconia, like silica, are readily reduced when the melting is carried out under hydrogen. Alloys, rather than pure metals, are the result and one would expect to find water vapor in the hydrogen gas passing over the melt.

As a result of the great difficulty in eliminating reactions between samples and oxide crucibles we have been led to accept as a more satisfactory procedure the fusion of the iron sample in a graphite crucible. Fusion of the sample in contact with carbon does not, of course, permit attaching any significance to the relative amounts of CO₂ and CO evolved. The results of such analyses are expressed simply as per cent. by weight of oxygen, hydrogen, and nitrogen in the metal.

We have also found that analysis by fusion in graphite determines more completely the oxygen in a mild steel or a pure iron than does vacuum fusion of the same steel or iron in a refractory oxide crucible.

Assuming a complete removal of carbon from the steel sample during fusion in vacuum, further elimination of oxygen from the metal by continuing the heating under a pressure of 10⁻⁴ mm. of mercury (assumed to be a pressure due to oxygen) should not be expected. The solubility of oxygen in pure iron at 1600° C. is about 0.30 per cent. equivalent to 1.35 per cent. FeO.⁵ The dissociation pressure of FeO at that temperature has been calculated as of the order of 10⁻⁵ mm. of mercury.⁶ Therefore the removal of oxygen should not proceed even in a saturated solution of FeO in pure iron by melting under a pressure of the order of the minimum reached by Brace and Ziegler. Iron containing less than the saturation value of FeO would have

⁵ C. H. Herty, Jr. et al.: *Min. and Met. Investigations*, Bull. 34, Carnegie Inst. Technology (1927).

⁶ R. S. Dean: *Theoretical Metallurgy*, 159. 1924. New York, J. Wiley & Sons.

a correspondingly lower equilibrium pressure of oxygen and could not be made oxygen free.

It may also be pointed out that the work on vacuum fusion methods for determining gases as carried on by the late Professor Oberhoffer and his coworkers in Germany during the past 10 years has also progressed from fusion of the sample in an oxide crucible⁷ with the determination of CO and CO₂, through a modified method in which an iron-carbon alloy was added to the sample, still in an oxide crucible, with the determination simply of total oxygen,⁸ and ultimately has come to the fusion of the sample in a graphite crucible⁹ with the results of analyses expressed as oxygen and hydrogen.

C. S. WITHERELL, New York, N. Y. (written discussion).—It can be seen that the authors of this instructive paper were mainly concerned with the quantity and composition of the gas found in a particular class of iron and it appears, in order to satisfactorily accomplish their investigation, they were forced to devise a special furnace for the purpose. However, as is evident from the title, the authors recognize the value of the furnace for the study of gases in other metals.

To those who have to do with the refining of copper, it will occur that here is a method and a device for definitely determining the composition of the gas that appears in overpoled copper. Probably, the thought has already occurred to the authors.

What this gas is, has always been a question. Skowronski, in his paper on Relation of Sulfur to the Overpoling of Copper,¹⁰ probably throws the most light on the subject, but, so far as I know, the gas itself has not yet been caught and analyzed. I would suggest to the authors that they undertake this interesting and valuable investigation. They are better fitted to do so than anyone else; they have the special furnace, means of producing copper overpoled under refinery conditions, and the experience in manipulating their apparatus.

The phenomenon of swelling of overpoled copper upon freezing is due largely to the tacky or viscous nature of the deoxidized molten copper at its freezing point; the minute bubbles of liberated gas failing to coalesce rise slowly and fail to escape before the complete solidification of the copper takes place. Under these conditions the freshly poured bar of overpoled copper retains considerable gas, but it is possible that in time most of the originally contained gas escapes from the solid bar, hence, for purposes of investigation it is important to extract the gas shortly after pouring. A 13-lb. chunk such as the authors intimate can be melted in their furnace should contain quite an appreciable amount of the gas in question.

E. W. FELL, Aachen, Germany (written discussion).—I have read with great interest the paper of Messrs. Brace and Ziegler, particularly as some research commenced with the late Prof. Paul Oberhoffer of the Naumann-Institut für Eisenhüttenkunde der Technischen Hochschule at Aachen, upon the influence of gases in metals, especially oxygen in steel, resulted in my constructing a high-frequency induction

⁷ P. Oberhoffer and A. Beutell: Die Bestimmung der Gase im Eisen. *Stahl und Eisen* (1919) **39**, 1584.

⁸ H. Strauch and P. Oberhoffer: Bestimmung des Sauerstoffs nach dem Heiss-extraktionsverfahren. *Stahl und Eisen* (1925) **45**, 1559.

⁹ A private communication from Prof. W. Hessenbruch, in the course of a recent comparison of the fusion methods used at the Bureau of Standards and at the Institut für Eisenhüttenkunde at Aachen [See Bur. of Stds. *Tech. News Bull.* 128 (December, 1927)] states that this latest modification of the method will be published shortly in *Stahl und Eisen*.

¹⁰ *Trans.* (1919) **60**, 312.

vacuum furnace somewhat similar to that of the authors though differing in certain aspects.

It was required to prepare iron-oxygen and iron-oxygen-sulfur alloys in quantities up to about 3 lb. (1500 gm.) under conditions of high purity. The furnace constructed, of which a sketch is shown in Fig. 8, has operated well.¹¹ The connection with the vacuum pumps, the measuring pipette for introducing gases into the evacuated bell-jar and with the revolving drum (provided with window for observation and for optical temperature measurement of the bath) used for dropping solids into the melt, passed through the water-cooled head of the glass bell-jar. The remaining furnace connections passed through the thick glass base plate of the furnace, being suitably fixed to the plate with vacuum cement consisting of water-free glycerin and litharge.

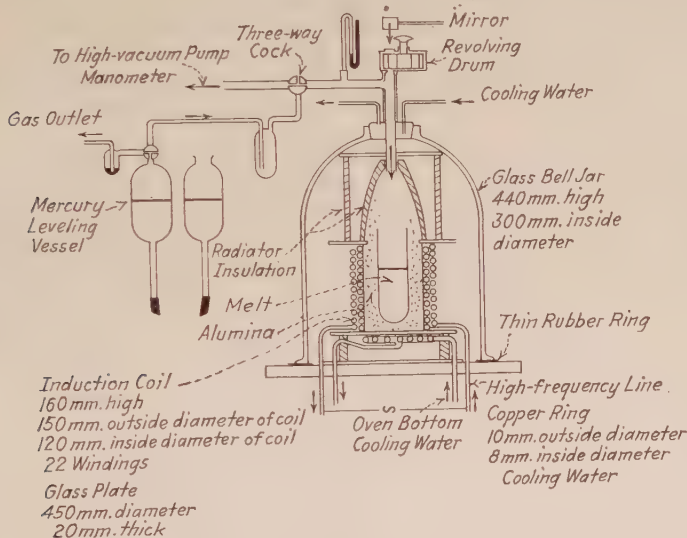


FIG. 8.—VACUUM HIGH-FREQUENCY FURNACE CONSTRUCTED BY E. W. FELL.

This type should prove a useful laboratory appliance where suitable high-frequency current is available, in view of its varied uses. The induced current causes a strong circulation of the molten metal bath, thus bringing about a thorough mixing action. This is also particularly favorable when for alloying purposes the material to be added to the melt is present as gas on the surface of the molten bath, or in the case when solids are to be dropped into the bath. A typical experiment in which $\frac{3}{4}$ l. of oxygen was passed into the evacuated bell-jar containing molten electrolytic iron (550 gm.) and allowed to remain in contact with the molten metal for 15 to 30 min. resulted in an increase in oxygen content in the iron in the cold state of 0.137 per cent.

The entire furnace was covered during operation by a large wooden box as shield against flying glass in case of accident. The writer has recently heard of a furnace of this type proving dangerous owing to an explosion of the glass bell-jar.

W. HESSENBRUCH, Aachen, Germany (written discussion).—The value of this very interesting work lies in the experiment to remove larger amounts of gas than is generally done in the proper methods of analysis. The difficulties increase greatly with the

¹¹ For further details see *Arch. d. Eisenhüttenw.* (1927–28) **10**, 659.

increasing weight of the samples. However, under these circumstances, it does not seem to me to be necessary to work with such an extraordinarily large apparatus. Anyone who has ever determined gases in metals knows that the simplicity and suitability of the experimental arrangements should be as great as possible, in order to obtain reliable results. The large internal surface of the entire apparatus is a constant source of error in view of the fact that the quantities of gas are passed through it first moist, and then dry. The paper does not state how the numerous parts of the apparatus were connected. According to my experience, the connection with vacuum tubing is not sufficient for this purpose.

It is incomprehensible why the authors completely excluded the chemical analysis of the amounts of gas; aside from the extraordinarily long time for the method of determination used (estimated time at least 8 to 10 hr.) it is absolutely impossible to keep all parts of apparatus in which gases are measured, at the same temperature, and especially where there are very low temperatures in the vicinity of the gas produced. For the unobjectionable measurement of the amounts of gas, the gas temperature would have to be measured each time. The deviations mentioned, in the measurement of the same amount of gas in different spaces, must be traced back to this to some extent.

A further disadvantage of the pure physical method is the fact that we do not know exactly which gases have been condensed. The data obtained by the authors, that 0.4 per cent. carbon dioxide is condensed with the water, shows these difficulties very plainly. The final calculated amounts of hydrogen and carbon monoxide must be determined from three different measurements for each. As there is an error in each reading, in my opinion the accuracy suffers on account of the large number of measurements. I can hardly believe that liquid iron gives off elementary oxygen. The amounts indicated probably come from the furnace. The carbon dioxide and carbon monoxide also do not come from the iron, as many investigators have shown.¹² It is a case of reaction gases that form in larger amounts the more carbon and oxides are present simultaneously. It is incomprehensible why the formation of carbon monoxide or carbon dioxide has not led to the disappearance of the carbon or the oxygen as it should theoretically. It is seen, from melting experiments with electrolytic iron in a current of hydrogen, that during this treatment oxygen is given off, and upon subsequent melting oxygen and carbon were given off (0.35 per cent. oxygen, 0.023 per cent. carbon). On heating for the second time after treatment with hydrogen, Armco iron no longer gave off carbon and oxygen. Here it seems that the previous treatment with hydrogen removed either all of the oxygen or all of the carbon. It is not clear why no hydrogen at all was found.

The determination of the empty value of the crucible is not sufficiently reliable. The amounts of gas coming from different crucibles varied greatly and represent one-fourth to one-fifth of the gases coming from the metal. Thus the empty value must

¹² E. Piwowarsky: Der Zeitpunkt der Siliziumgabe in seiner Wirkung auf die physikalischen Eigenschaften und den Gasgehalt von Martin-flußeisen. *Stahl und Eisen* (1920) **40**, 773.

E. Maurer: *Festschrift d. K. W. Gesellschaft Berlin* (1921) 146.

P. Oberhoffer and E. Piwowarsky: Zur Bestimmung der Gase in Eisen. *Stahl und Eisen* (1922) **42**, 801.

P. Oberhoffer, E. Piwowarsky, E. Pfeiffer-Schiessl and H. Stein: Über Gas und Sauerstoffbestimmungen in Eisen, ins besondere Guss Eisen. *Stahl und Eisen* (1924) **44**, 113.

P. Klinger: Die Bestimmung der Gase in Eisen und Stahl. *Stahl und Eisen* (1926) **46**, 1245, 1284, 1353.

depend greatly on the carbon content of the metal, as at 1600° this reacts with the refractory oxides in vacuum.¹³

The assumption that the increased liberation of gas before melting depends on a decreased solubility at the A₄ point, contradicts my experience. The strong evolution of gas is explained only by the diffusive power increasing strongly below the melting point. I would like to suggest that the authors check the results obtained in a physical method by a chemical analysis of the gas, either gravimetrically or volumetrically.

C. E. PLUMMER, New York, N. Y.—Our experiences at the Union Carbide & Carbon Research Laboratories confirm the recent statement that the refractory materials do play an important part in the study of gases in metals. We have found that a reaction takes place between the molten metal and crucibles made of either aluminum oxide or magnesium oxide. Our laboratory was the first to install the vacuum fusion method as developed by Jordan and Eckman at the Bureau of Standards for the determination of gases in metals. During the development of the method, various oxide crucibles were used and were found to react with the carbon present in the steel. Graphite is used when the total oxygen content of a metal is desired.

Some time ago we had occasion to determine the oxygen content of a sample of copper containing silicon and copper oxide. Although the copper was melted in a vacuum in a graphite crucible, all the oxygen was not removed as carbon monoxide, but part was recovered as silica on the surface of the frozen ingot. The copper oxide was not all reduced, probably due to the insolubility of carbon in copper. Undoubtedly, the copper oxide was reduced only where the molten metal came in contact with the walls of the hot graphite crucible. The silicon also acted as a reducing agent, forming silica on the surface of the copper.

We made up a series of low-carbon alloys, containing varying amounts of chromium and iron. These alloys were made using electrolytic chromium and electrolytic iron and were melted in magnesium oxide crucibles. Although no difficulty was encountered in making low-carbon alloys, the chromium was found to be badly oxidized and thus partly lost during the melting. Several tenths of a per cent. of carbon were added to several heats, with the result that the alloy was found to contain less than 0.01 per cent. carbon. The ingots were allowed to freeze in the crucible and in each case were covered with chromium oxide. Since the alloys were melted quickly *in vacuo*, we were led to believe that the chromium reduced the magnesium oxide. Small amounts of manganese, silicon and zirconium were added, but none of these was recovered in the finished heat.

These few remarks are made in order to show why we believe that molten metal reacts with the crucible and gives results different from what might be expected.

R. C. DALZELL, Baltimore, Md.—We have started at Harvard University an investigation of factors affecting absorption of gases in refined copper. This was undertaken at the request of the American Smelting & Refining Co., which is cooperating very closely with the metallurgical department of the university in this work. Attention will be confined almost entirely to items of practical value. As progress is made, it is intended to present the results to the Institute in the form of a series of papers.

P. H. BRACE and N. A. ZIEGLER (written discussion).—The authors will agree with Mr. Plummer as to the tendency for reaction to take place between the crucible material and the components of the melt, particularly carbon, and feel as he does that

¹³ L. Jordan and J. R. Eckman: *Op cit.*

W. Hessenbruch and P. Oberhoffer: Sauerstoff in Eisen und Stahl. *Arch. d. Eisenhüttenw.* (1927) 1, 57.

this may be a source of serious error in some cases. There are two ways to deal with this problem: first, to choose a crucible material such that reactions will go to completion; second, to arrange matters so that reactions will be reduced to a point where their effects will be unimportant. Jordan and Eckman have chosen the former method. They were interested primarily in estimating the total content of gaseous elements, and carbon provided an effective means for displacing gases from combination as well as solution. We chose the latter method because we were particularly interested in obtaining direct correlation between the quantities of gas *present as such* and peculiarities in the physical properties of the samples of metal which we melted. Hence the use of a graphite crucible was out of the question because the properties of all alloys that will dissolve carbon, even to a small extent, are markedly affected by the presence of this element. Our problem therefore has been to establish conditions such that reaction between crucible and melt would be least rapid, and we feel at this time that the best means of accomplishing this is to proceed as far as practical difficulties will permit along the lines noted below.

- (1) Reduction of gas pressure in furnace chamber.
- (2) Increase of chemical stability and refractoriness of crucible material.
- (3) Increase of ratio of weight of metal to weight of refractories and contact area of metal and refractories.

We believe that the importance of a good vacuum is not generally recognized. Oxidation of iron will occur at pressures below 0.001 mm. of mercury, and we strive to keep the final pressure in our furnace down to 0.0001 mm. of mercury. The gas pressure in the furnace appears to have a direct bearing on reactions between the crucible and the melt. For example, silica may be brought to fusion in a graphite crucible without appreciable reaction if the graphite has been thoroughly degasified and if the heating is done in a high vacuum. It appears probable that the marked oxidation which occurred in the case of Mr. Plummer's chromium alloys was due to some defect in his pumping or vacuum system, rather than to the reduction of the magnesium oxide of his crucible. We base this view of the matter on the fact that we have prepared, from practically carbon-free raw materials, ingots of high-chromium alloy which showed no evidence of oxidation.

Corrosion of Metals as Affected by Time and by Cyclic Stress*

BY D. J. McADAM, JR., † ANNAPOLIS, MD.

(New York Meeting, February, 1928)

PART I. OUTLINE OF INVESTIGATION, DESCRIPTION OF MATERIAL AND METHODS •

RESULTS of investigation of corrosion-fatigue of metals at the U. S. Naval Engineering Experiment Station, Annapolis, Md., have been discussed by the writer in several recent papers.^{1,2,3,4} In those papers references were also given to the work of Haigh in 1917.⁵ Efforts by the writer to obtain a better understanding of some of the factors involved in corrosion-fatigue finally developed into a general investigation of the effect of time and cyclic stress on corrosion of metals.

Corrosion-fatigue of Metals

As described in the papers mentioned, rotating-cantilever specimens, conically tapered so that the stress is nearly uniform over a length of about 1.5 in., were subjected to simultaneous fatigue and corrosion. For this purpose a stream of water was diagonally applied so as to sweep the specimen from the outer to the inner fillet and surround the stressed surface with water. The fresh water is a calcium carbonate water, the composition of which has been given in a previous paper.² The salt water is Severn River water having a saline content about one-third that of sea water.

The previous papers described results obtained with ferrous and non-ferrous metals. The experiments showed that even slight corrosion simultaneous with fatigue may cause failure at nominal stresses far

* Published by permission of the Secretary of the Navy.

† Metallurgist, U. S. Naval Engineering Experiment Station.

¹ D. J. McAdam, Jr.: Stress-strain-cycle Relationship and Corrosion-fatigue of Metals. *Proc. Am. Soc. Test. Mat.* (1926) **26**, 224.

² D. J. McAdam, Jr.: Corrosion-fatigue of Metals as Affected by Chemical Composition, Heat-treatment and Cold Working. *Trans. Am. Soc. Steel Treating* (1927) **11**, 355.

³ D. J. McAdam, Jr.: Corrosion-fatigue of Non-ferrous Metals, *Proc. Am. Soc. Test. Mat.* (1927) **27**, Pt. 2.

⁴ D. J. McAdam, Jr.: Fatigue and Corrosion-fatigue of Metals, *Proc. of Internat'l Congress for Testing Materials*, Amsterdam, September, 1927.

⁵ B. P. Haigh: Experiments on the Fatigue of Brasses. *Jnl. Inst. Metals* (1917)

below the ordinary endurance limit. It was also shown that severe stressless corrosion prior to fatigue is usually much less damaging than even slight corrosion simultaneous with fatigue. The relative effect of prior stressless corrosion on the fatigue limit, however, varies with the electrolytic potential of the alloy. The term "corrosion-fatigue" has been restricted to mean the simultaneous action of fatigue and corrosion. The action of corrosion followed by fatigue has been called "prior-corrosion fatigue."

A stress-cycle graph representing corrosion-fatigue is a curve approaching a horizontal asymptote, which may be called a "corrosion-fatigue limit." It was shown in the previous papers^{3,4} that the corrosion-fatigue limit apparently depends more on electrochemical than on physical properties. Chemical composition, heat-treatment, and cold working have little effect unless there is a corresponding change in corrosion-resistance. The corrosion-fatigue limit seems to depend chiefly on corrosion resistance.

A tentative analysis of the corrosion-fatigue process was given by the writer in a preceding paper.⁴ According to this analysis, if the initial stress is below the endurance limit, but above the corrosion-fatigue limit, the corrosion-fatigue process is divided into two stages. The first stage is the formation of pits. As the stress is below the endurance limit, such pit formation is evidently due to electrolytic solution pressure; not to fatigue. The electrolytic solution pressure that causes the pitting, however, is an enhanced solution pressure due to cyclic stress. The apparent enhancement of solution pressure by cyclic stress may be due in part to continual breaking of the surface film, but may also be due in part to actual increase in solution pressure due to the stress. Whatever may be the reason, a metal behaves as if its solution pressure were increased by cyclic stress. Of this the phenomena of corrosion-fatigue are evidence.

As the pit progresses there is intensification both of actual stress and solution pressure. The intensification of stress is due to the usual stress concentration at an abrupt change of section. The intensification of solution pressure is due to the intensification of stress.

The mutual intensification of solution pressure and stress continues until the actual stress at the advancing edge of the pit surpasses the endurance limit. The second stage in corrosion-fatigue then begins. This second stage is merely fatigue accelerated by corrosion. In this stage the crack advances at a continually accelerated rate until the specimen breaks.

The interrelationship of the two stages of corrosion-fatigue depends largely on the depth and sharpness of the pits formed in the first stage. The depth and sharpness of the pits depend not only on the natural susceptibility of the alloy to corrosion-pitting (the electrolytic potential is usually an index of this susceptibility) but also on the influence of cyclic

stress on corrosion-pitting. Little has heretofore been known about the influence of cyclic stress on corrosion-pitting, therefore an investigation of this subject was started at the Naval Engineering Experiment Station.

Outline of Continued Investigation

In this investigation of the effect of cyclic stress on corrosion, the stresses used were below the corrosion-fatigue limit. The results of the investigation, therefore, should lead to a better understanding, not only of corrosion-fatigue, but also of the behavior of metals under ordinary service conditions, in which the cyclic stresses do not exceed the corrosion-fatigue limit. Though the alloy under such conditions does not fail, this fact gives no assurance that the factor of safety is not greatly reduced.

In this paper the effect of corrosion on the fatigue limit is the effect that has been given chief consideration. Using the fatigue limit of the corroded specimen as a criterion, an investigation has been made of the effect of time and cyclic stress on corrosion.

Specimens were corroded at various cyclic stresses from zero to the corrosion-fatigue limit, for various times, and at various cycle frequencies. They were then oiled and subjected to fatigue in air. Each experiment, therefore, consisted of two stages, a pitting stage and a fatigue stage. Such experiments may be called "prior-corrosion-fatigue" tests. In a prior-corrosion-fatigue test the nominal stress in the pitting stage is usually lower than in the fatigue stage. In this respect a prior-corrosion fatigue test differs from a corrosion-fatigue test.

In future discussion of prior-corrosion fatigue the pitting stage will be called the "first stage" or "stage 1;" the fatigue stage will be called the "second stage" or "stage 2."

In these prior-corrosion fatigue tests, as in the corrosion-fatigue tests described in previous papers,^{1,2,3,4} the specimens were corroded in a water stream, which was diagonally applied so as to surround with water the tapered portion of the specimen. In stage 1 the specimen usually was revolved at 1450 r. p. m. In some experiments, however, the specimen in stage 1 was revolved at lower speed. In stage 2 the specimen was revolved at 1450 r. p. m.

In addition to these prior-corrosion fatigue tests, ordinary fatigue and corrosion-fatigue tests were made with each material.

Machines and Specimens

The rotating cantilever machines and specimens have been described in previous papers.^{6,7} The conically tapered specimen is so designed

⁶ D. J. McAdam, Jr.: Endurance of Steels under Repeated Stress. *Chem. Met. Eng.* (Dec. 14, 1921) **25**, 1081.

⁷ D. J. McAdam, Jr.: Endurance Properties of Alloys of Nickel and of Copper. *Trans. Am. Soc. Steel Treating* (1925) **7**, 54, 217, 581.

TABLE 1.—*Chemical Composition*
All Values are Averages of at Least Four Determinations

Alloy	Material Designation	C Per Cent.	S Per Cent.	P Per Cent.	Mn Per Cent.	Si Per Cent.	Cr Per Cent.	Ni Per Cent.	V Per Cent.	Cu Per Cent.	Al Per Cent.	Fe Per Cent.	Mg Per Cent.
Chrome vanadium steel.....	AZ	0.46	0.010	0.007	0.69	0.24	0.88	20.68	0.14	0.10			
Medium chromium-high nickel steel.....	HS	0.45	0.021	0.017	0.57	1.01	8.05	0.23		0.07			
Stainless steel.....	GS	0.38	0.012	0.017	0.26	0.20	14.50	0.81					
Aluminum bronze, rolled.....	IA				0.14						*7.49	2.89	
Monel metal, cold-drawn.....	IU	0.090	0.026	0.013	1.00	0.009		*71.30		88.67		1.83	
78:21 copper-nickel, cold-worked.....	HE	0.031	0.011	0.007	0.29	0.005		*21.24		25.72		0.51	
97:3 copper-nickel, cold-drawn.....	ID		0.011		0.04			2.72		77.92		0.04	
Copper, electrolytic, hot-rolled.....	EE									97.27		0.004	
Copper, electrolytic, cold-worked.....	HF									*99.996		0.004	
Aluminum, hard temper.....	IMB				0.003	0.13				*99.996		0.004	None
Aluminum-manganese, hard temper.....	ILB				1.33	0.28				0.10	*99.47	0.31	None

* By difference.

that the maximum stress is $\frac{3}{4}$ in. out from the inner fillet, and the stress varies only about 1.5 per cent. over a length of 1.5 in. With this specimen, therefore, a comparatively large region may be subjected to simultaneous corrosion and cyclic stress.

The method of alternate longitudinal and transverse polishing of this specimen has been previously described.⁶ The surface finish by this method is sufficiently smooth to permit examination of the structure at a magnification of 100. Details of machining and polishing are tabulated and kept on file at the Naval Engineering Experiment Station. This information is available for those who are interested.

Material

Ferrous and non-ferrous alloys were used in this investigation. Material was generously supplied by the International Nickel Co., the Aluminum Co. of America, the American Brass Co., the Firth-Stirling Steel Co., the Universal Steel Co., and the Alcumite Corp'n. (a division of the Duriron Co.). All the material was in the form of 1-in. round bars.

Chemical Composition

The chemical composition of the alloys used is given

TABLE 2.—*Heat Treatment*

Alloy	Material Designation	Heated to Deg. F.	Time Held Min.	Cooled in	Reheated to Deg. F.	Time Held Min.	Cooled in
Chrome vanadium steel.....	‡AZ-0-7.5	1575	60	Oil	750	60	Furnace
Chrome vanadium steel.....	‡AZ-0-10	1575	60	Oil	1000	60	Furnace
Chrome vanadium steel.....	‡AZ-15.75	1575	60	Furnace			
Medium chromium-high nickel steel.....	*HS	As received					
Stainless steel.....	GS-0-10.75	1800	60	Oil	1075	120	Air
Stainless steel.....	GS-0-12	1800	60	Oil	1200	120	Air
Stainless steel.....	GS-17	1700	60	Furnace			
Aluminum bronze, rolled.....	IA	As received					
Monel metal, cold-drawn.....	IU-8	800	180	Furnace			
78:21 Copper-nickel cold-worked.....	HE-4	400	180	Furnace			
78:21 Copper-nickel cold-worked.....	HE-14	1400	60	Furnace			
97:3 Copper-nickel, cold-drawn	‡ID	As received					
Copper, electrolytic cold-worked.....	HF-2.5	250	180	Furnace			
Copper, electrolytic hot-rolled	EE-12	1200	60	Furnace			
Aluminum, hard temper.....	‡IMB	As received					
Aluminum-manganese, hard temper.....	‡ILB	As received					

‡ Previously heated to 1700° F., held 60 min. and cooled in air.

* Annealed by manufacturer.

§ Some specimens were annealed at 600° F. in order to relieve internal stress. There was practically no difference in physical properties.

† Heat treated by manufacturer.

in Table 1. Trade names, except those that are in universal use, have been avoided and each material has been designated by a combination of letters.

Heat Treatment

Details of heat treatment are given in Table 2.

Tension and Charpy Tests

Results of tension and Charpy impact tests are given in Table 3. In this table, "elastic limit" means the highest stress that leaves no appreciable permanent deformation after removal of the load. "Proof stress" means the stress that results in a permanent deformation of 0.0001 in. per inch of length after removal of the load.

TABLE 3.—Static Tension and Charpy Impact Test Results, Averages and Mean Departures from Averages

Alloy	Condition	Material : Designa- tion	Tensile : strength	Johnson's : limit	Proof : stress	Elastic : limit	Proportional : limit	Elonga- tion in: 2 in.	Charpy : impact value, ft.-lb.
Chrome Vanadium Steel	Quenched & Drawn	AZ-O-7.5	179300 ± 4500	126500 ± 5600	129200 ± 5300	110000 ± 10000	14.0 ± 1.0	47.8 ± 3.9	5.7
"	"	AZ-O-10	150500 ± 4700	122300 ± 2500	121900 ± 3100	111000 ± 4500	17.1 ± 0.8	54.3 ± 1.3	17.7
"	Annealed	AZ-15.75	96800 ± 1350	57000 ± 2000	57000 ± 2000	50000 ± 3800	27.3 ± 1.3	53.6 ± 1.0	17.1
Medium Chromium - High Nickel Steel	As Received	HS	118100 ± 2900	43900 ± 2400	42900 ± 600	32000 ± 3000	31.0 ± 2.3	55.7 ± 1.2	32.5
Stainless Steel	Quenched & Drawn	CS-O-10.0 ^a	178100 ± 1900	126700 ± 7600	119000 ± 101700	66700 ± 2200	13.0 ± 1.7	40.2 ± 0.3	4.9
"	"	CS-O-12	117400 ± 4200	53200 ± 8600	56000 ± 6000	45000 ± 2000	21.0 ± 1.7	52.3 ± 0.6	13.4
"	Annealed	CS-17	94400 ± 1600	40000 ± 2500	39600 ± 1200	37500 ± 2500	29.6 ± 2.3	61.3 ± 1.1	26.8
Aluminum Bronze, Rolled	As Received	1A	90400 ± 800	41700 ± 1100	45300 ± 9400	31700 ± 2200	34.7 ± 1.4	35.8 ± 6.4	21.9
Monel Metal, Cold-Drawn	Low Anneal	1U-6	63500 ± 500	52500 ± 300	52800 ± 300	44000 ± 1000	36.5 ± 0.5	70.5 ± 1.8	63.00
78:21 Copper-Nickel, Cold-Worked	"	HE-4	62400 ± 200	44700 ± 1800	44700 ± 1100	34300 ± 1800	24.7 ± 1.0	56.2 ± 0.8	1.4
"	Annealed	HE-14	47300 ± 600	11000 ± 700	11700 ± 1500	8100 ± 1200	50.0 ± 1.7	74.7 ± 1.3	1.3
97:3 Copper-Nickel, Cold-Drawn	As Recd. & Low Anneal	ID and ID-6	47000 ± 1300	35700 ± 700	34400 ± 2100	27500 ± 4100	13.9 ± 0.3	73.5 ± 0.9	40.9
Copper, Electrolytic, Cold-Worked	Low Anneal	HP-2.5	46500 ± 200	31000 ± 700	21200 ± 1100	9200 ± 600	14.5 ± 0.6	55.8 ± 2.1	0.18.0
Copper, Electrolytic, Hot-Rolled	Full Anneal	EP-12	31200 ± 31200	—	—	3000 ± 3000	73.8 ± 0.3	52.8 ± 1.1	1.1
Aluminum, Hard Temper	As Received	TMB	20800 ± 200	15000 ± 200	15000 ± 200	12500 ± 500	15.6 ± 0.5	63.0 ± 0.6	16.1
Aluminum-Manganese, Hard Temper	"	1LB	27500 ± 400	20000 ± 500	16500 ± 500	11500 ± 500	11.0 ± 0.5	39.3 ± 0.3	9.1

Unless otherwise indicated each value is the average of two determinations.

^a Stress-strain graph curved from origin.^c Average of three determinations.^d Average of five determinations.^e Average of six determinations.

PART II. EFFECT OF CYCLIC STRESS ON CORROSION OF CHROME-VANADIUM STEEL

Fatigue and Corrosion-fatigue of Chrome-vanadium Steel

In Fig. 1 are shown results of numerous prior-corrosion fatigue tests of chrome-vanadium steel. For comparison, fatigue and corrosion-fatigue graphs for the same material have also been included; these graphs are taken from a previous paper.⁴ To avoid obscuring results of prior-corrosion fatigue tests, individual results of fatigue and corrosion-fatigue tests have been omitted, and the results have been represented only by stress-cycle lines. Fatigue of uncorroded specimens is represented by the heavy solid lines *A*, and corrosion-fatigue in fresh water is represented by the broken lines *B*.

Fig. 1*a* represents fully annealed material. Fig. 1*c* represents material that was drawn at a comparatively low temperature after quenching, thus producing a steel of spring temper. Fig. 1*b* represents material that was drawn at a higher temperature. Details of heat treatment are given in Table 2 and physical properties are given in Table 3.

Each series of graphs has its own logarithmic scale of abscissas, which is indicated by figures along the graph. For all three series the scale of ordinates is the same. Beside each stress-cycle graph there are indicated some of the strength values as determined by tension test. These are represented by the following symbols: tensile strength, T. S.; Johnson's limit, J. L.; proof stress, P. S.; elastic limit, E. L.; proportional limit, P. L.

The fatigue graphs *A* as usual are curves descending toward a horizontal asymptote, the endurance limit. As usual, the endurance limits of the quenched and tempered steel are considerably higher than that of the fully annealed steel. For the hardest steel, AZ-0-7.5, however, the ratio of endurance limit to tensile strength (endurance ratio) is somewhat lower than for materials AZ-0-10 and AZ-15.75.

The corrosion-fatigue graphs *B* also are curves descending toward a horizontal asymptote, the corrosion-fatigue limit. It will be observed that the corrosion-fatigue limit is considerably lower for the quenched and tempered steel than for the fully annealed steel. As has been pointed out in previous papers,^{1,2,3,4} the corrosion-fatigue limit of steels, except low-carbon steels, is not improved, but may actually be lowered by heat treatment.

For the spring steel, AZ-0-7.5, the fresh-water corrosion-fatigue limit is only about one-fifth the endurance limit. The rapidity with which corrosion-fatigue manifests itself with steel of this kind is illustrated by the steep descent of the corrosion-fatigue graph *B* between abscissas of 100,000 and 2,000,000 cycles, which corresponds to a range of time from 1.25 to 24 hr.

STAGE 1 STRESSES AND CYCLES

Fig. 1a			Fig. 1b			Fig. 1c		
Symbol	Fresh Water		Symbol	Fresh Water		Symbol	Fresh Water	
	Stress, Lb. per Sq. In.	Cycles, Millions		Stress, Lb. per Sq. In.	Cycles, Millions		Stress, Lb. per Sq. In.	Cycles, Millions
A	11,000	20.2	A	Zero	20.0	A	Zero	20.0
B	11,000	19.8	B	Zero	20.1	B	Zero	20.0
C	15,000	20.2	C	2,500	20.4	C	2,000	20.4
D	2,500	19.8	D	2,500	21.2	D	6,000	21.7
E	Zero	20.0	E	2,500	20.4	E	6,000	20.4
F	11,000	20.2	F	5,000	22.1	F	6,000	22.6
G	15,000	20.0	G	5,000	20.3	G	8,000	20.1
H	11,000	21.0	H	6,000	20.2	H	8,000	22.6
I	11,000	20.1	I	6,000	20.3	I	8,000	21.6
J	20,000	20.6	J	7,000	20.9	J	9,000	20.8
K	19,000	20.6	K	7,000	21.2	K	10,000	20.4
L	20,000	20.5	L	7,000	21.3	L	10,000	20.1
M	18,000	20.1	M	7,000	19.7	M	10,000	22.3
N	6,000	19.8	N	7,000	20.4	N	10,000	20.0
O	6,000	20.8	O	9,000	22.3	O	10,000	20.1
P	2,500	20.8	P	9,000	20.2	P	10,000	20.0
Q	6,000	19.9	Q	9,000	20.3	Q	10,000	20.8
R	8,000	19.5	R	9,000	20.0	R	10,000	21.2
			S	9,000	20.1	S	13,000	22.0
			T	9,000	20.8	T	13,000	21.0
			U	13,000	21.6	U	13,000	19.8
			V	13,000	20.7	V	13,000	20.6
			W	13,000	19.8	W	13,000	20.2
			X	13,000	20.5			
			Y	13,000	20.3			
			Z	13,000	20.7			
			a	13,000	20.0			
			b	15,000	19.6			
			e	15,000	20.6			
			g	15,000	20.6			
			h	15,000	20.4			
			k	11,000	19.4			

Effect of Stressless Corrosion

Each small square or inverted triangle in Fig. 1 represents by its position the result of the second or fatigue stage of a prior-corrosion fatigue test. Each square represents the result of stressless corrosion followed by fatigue in air. During corrosion the specimen was revolved at 8 r. p. m. in a stream of fresh water. In the subsequent fatigue test it was revolved at 1450 r. p. m. The small numerals beside each square indicate the corrosion time in days. Each zigzag line shown in these

figures represents the course of a prior-corrosion fatigue test in which the stress was raised at intervals until the specimen failed. The lower end of the zigzag line represents the original stress and the number of cycles endured at this stress. The course of the line represents the stress increases and the cycle intervals at which these increases were made.

Through each series of squares representing approximately the same corrosion time, a dotted line has been drawn. The distance of this dotted line below the heavy solid line *A* is a measure of the effect of prior stressless corrosion for the time indicated. It will be observed that the effect of one day's stressless corrosion is relatively large. With increase in corrosion time, however, the effect of each additional day becomes less. Beyond about 10 days the effect of increase in corrosion time is evidently slight. It should be noted that 10 days' corrosion time corresponds approximately to the abscissa, 20,000,000 cycles, at which the corrosion-fatigue graph *B* becomes approximately horizontal. (At 1450 r. p. m., the cycle frequency used in obtaining the corrosion-fatigue graph, each day's time corresponds to about 2,000,000 cycles.) For this steel, 10 days' stressless corrosion lowers the fatigue limit about half as much as does corrosion-fatigue for the same time.

Effect of Prior Corrosion at Stresses Varying from Zero to the Corrosion-fatigue Limit

The small inverted triangles in Fig. 1 represent results of prior-corrosion fatigue tests in which the stage 1 stress varies from zero nearly to the corrosion-fatigue limit. The position of each triangle represents the result of a stage 2 test. Adjacent to each triangle is a key letter. The same key letter in a list accompanying Fig. 1 indicates the stage 1 stress and number of cycles.

In stage 1 the specimens were revolved at 1450 r. p. m. in a stream of fresh water for approximately 20,000,000 revolutions; about 10 days' time. With increase in corrosion time, as stated above, the increase in effect of corrosion would be very slight. By corroding the specimens, therefore, for a constant time of 10 days, but at various stresses, the influence of all other variables except stress has been minimized.

Each light solid line in Fig. 1 is a stage 2 graph corresponding to a definite stage 1 stress, which is indicated by the number at the right of the line. It will be observed that the light solid line designated "zero," and representing the effect of stressless corrosion at 1450 r. p. m., is slightly above the corresponding dotted line representing the effect of stressless corrosion for the same time at 8 r. p. m. The corrosion conditions were possibly less severe in the former case than in the latter. This may have been due to some difference in the adjustment of the water stream in the two different machines.

The uppermost stage 2 graphs in Fig. 1 are curves with horizontal asymptote and nearly parallel to the endurance graph *A*. As the stage 2 graph is lowered, however, the slope at the left becomes steeper, the lower portion becomes more nearly horizontal, and the connecting curve becomes shorter. The graph now resembles, and actually is, a graph obtained with notched specimens. The difference in form between these stage 2 graphs and the corrosion-fatigue graph *B* is due largely to the fact

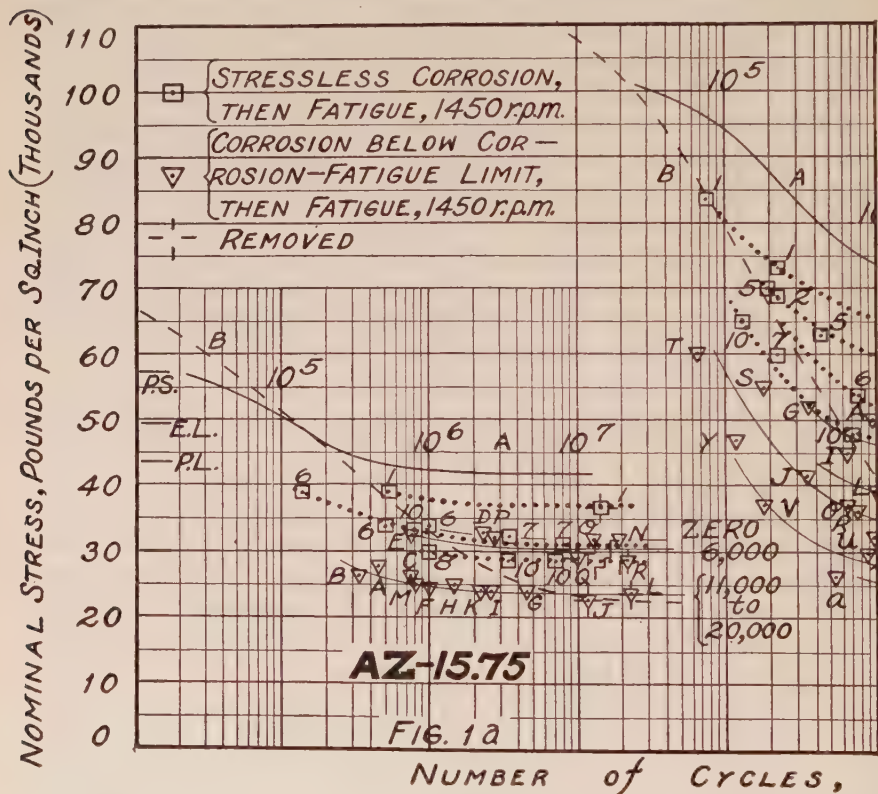
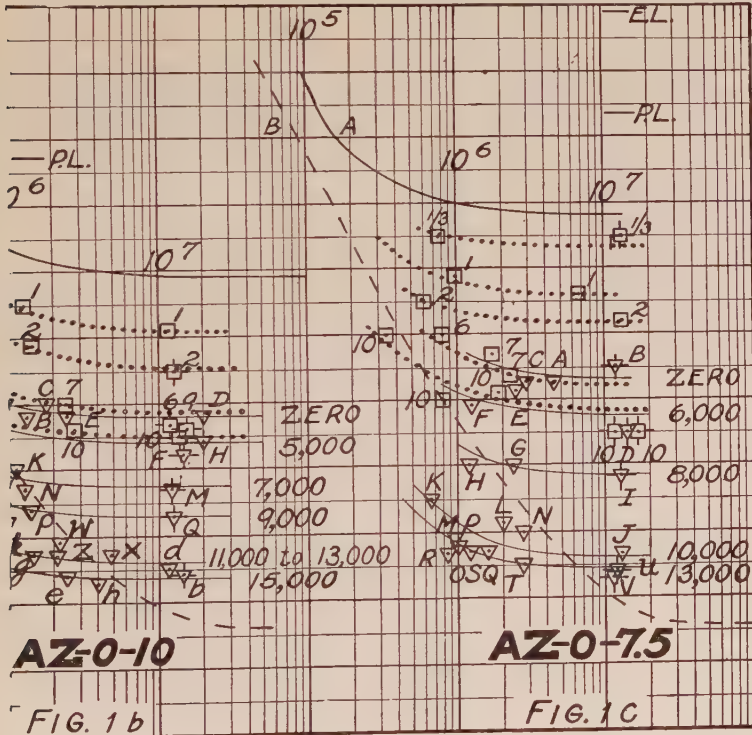


FIG. 1.—CORROSION OF CHROME-VANADIUM

that each of the former graphs represents constant corrosion time, whereas the latter graph represents varying corrosion time.

As the stress in stage 1 increases, the fatigue-limit stress in stage 2 decreases. The two stresses would evidently meet and coincide at the corrosion-fatigue limit. As illustrated in Fig. 1, however, the descent of the stage 2 graph with increase in the stage 1 stress is not uniform or regular. As shown in Fig. 1c, the position of the stage 2 graph is lowered very little with increase in the stage 1 stress from zero to 6000. With increase of the stage 1 stress from 6000 to 8000, the descent of the stage 2 graph is much greater. With further increase in the stage 1 stress from

8000 to 10,000 the descent of the stage 2 graph is still greater. An increase from 8000 to only 9000 in the stage 1 stress has more than twice as much effect on the stage 2 graph as does an increase of the stage 1 stress from zero to 6000. Above 9000 or 10,000, further increase in the stage 1 stress to 13,000 or 14,000 has little effect on the position of the stage 2 graph. At, and just below, the corrosion-fatigue limit the stage 2 graph evidently again becomes sensitive to slight changes in the stage 1 stress.



LOGARITHMIC SCALE
STEEL AS AFFECTED BY CYCLIC STRESS.

Fig. 1b shows a similar irregularity in the descent of the stage 2 graph with increase in the stage 1 stress. The stage 2 graph is relatively insensitive to changes in the stage 1 stress between zero and 5000 or 6000, is evidently very sensitive to changes in the stage 1 stress between 7000 and about 11,000, and is insensitive to changes in the stage 1 stress between about 11,000 and 15,000.

Fig. 1a shows a similar, but more striking irregularity in the behavior of the fully annealed steel. With increase of stage 1 stress from zero to 6000, the stage 2 graph is lowered very little. With increase of stage 1 stress from 6000 to 11,000, the stage 2 graph descends nearly to the cor-

rosion-fatigue limit. With further increase of stage 1 stress by several steps from 11,000 to 20,000, the position of the stage 2 graph is practically unchanged.

The three sets of stage 2 graphs in Fig. 1, therefore, agree in indicating that there is a surprising irregularity in the descent of the stage 2 graph with increase in the stage 1 stress from zero to the corrosion-fatigue limit. Reasons for this irregularity will be discussed later.

Relationship between Stress in Stage 1 and Nominal Fatigue Limit in Stage 2

Relationship between stage 1 and stage 2 is illustrated by Fig. 2. In this figure, abscissas represent stage 1 stresses and ordinates represent the stage 2 nominal fatigue limits as taken from Fig. 1. The abscissa scale is twice the ordinate scale. In addition to the three graphs representing chrome-vanadium steel, Fig. 2 contains other graphs, which will be described later.

As explained above, at the corrosion-fatigue limit the stage 1 stress and the stage 2 fatigue limit are the same. For this reason each point (marked L in Fig. 2) representing a corrosion-fatigue limit is so placed that its abscissa and ordinate have the same value. A little consideration will show that the descent of each graph below the point L is nearly vertical. The abscissa at the lower end of each graph for steel in Fig. 2 is the same as the ordinate of the corresponding corrosion-fatigue graph in Fig. 1 at an abscissa of 20,000,000 cycles. At this stress a specimen tested in water for 20,000,000 cycles would fail. As, for such a specimen, there would be no stage 2, the corresponding ordinate in Fig. 2, is zero. Examination of the corrosion-fatigue graphs in Fig. 1 shows that the ordinate at 20,000,000 cycles is only slightly above the corrosion-fatigue limit. Hence the abscissa at the lower end of each graph in Fig. 2 is only slightly greater than the abscissa at the corrosion fatigue limit L . As stated above, therefore, the course of each graph in Fig. 2 below L is nearly vertical.

The three graphs for chrome-vanadium steel in Fig. 2 illustrate the relationship between stage 1 stress and stage 2 fatigue limit. The origin of each graph represents the fatigue limit after 10 days' stressless corrosion. As indicated in the figure, the origin of each graph is considerably below the point representing the endurance limit. As each graph extends to the right, the slope is at first slight, but gradually increases until between abscissas of about 6000 and 10,000 the slope is steep. Between abscissas of about 8000 and 9000 the three graphs are steepest, the graph for material AZ-0-7.5 being nearly vertical. Each graph then reverses its curvature, turns outward until it becomes nearly horizontal and remains so for a distance that is much greater for the fully annealed than for the quenched and tempered steel. As it nears

the point *L* representing the corrosion-fatigue limit, the graph again begins to curve downward. Below the point *L* it is nearly vertical.

The qualitative agreement in form of these three graphs makes it evident that the complicated form represents a real relationship between the stress in stage 1 and the fatigue limit in stage 2. Possible reasons for the abrupt reversal of curvature after the first steep descent of each graph will be discussed later.

Relation between Cyclic Stress in Stage 1, and Stress Concentration in Stage 2

As the lowering of the fatigue limit by corrosion pitting is evidently due to stress concentration it seemed desirable to study the relation

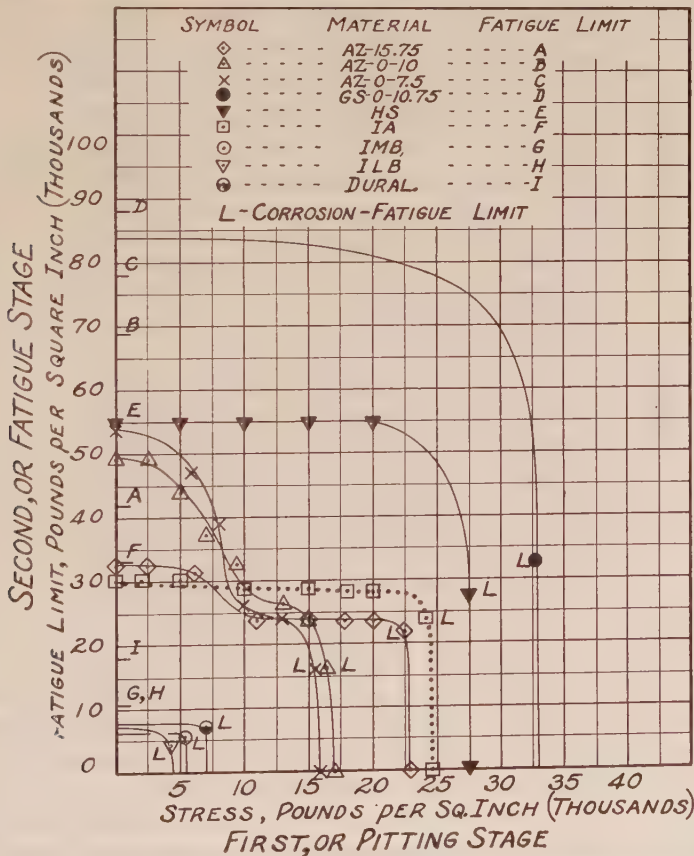


FIG. 2.—RELATION BETWEEN CYCLIC STRESS IN STAGE 1 AND FATIGUE LIMIT IN STAGE 2, FOR VARIOUS METALS.

between cyclic stress in stage 1 and the resulting stress concentration due to corrosion pitting.

Assuming that the actual endurance limit of the metal at the bottom of a corrosion pit remains unchanged, the ratio of the actual stress at the bottom of the pit to the nominal stress in the specimen may be obtained by dividing the fatigue limit of the uncorroded specimen by the fatigue limit of the pitted specimen. This ratio will be called the "stress-concentration ratio." In this calculation of the stress-concentration ratio there is an error due to neglect of the decrease in effective diameter of the specimen due to pitting. In specimens of the size used in this investigation, however, this error is evidently small.

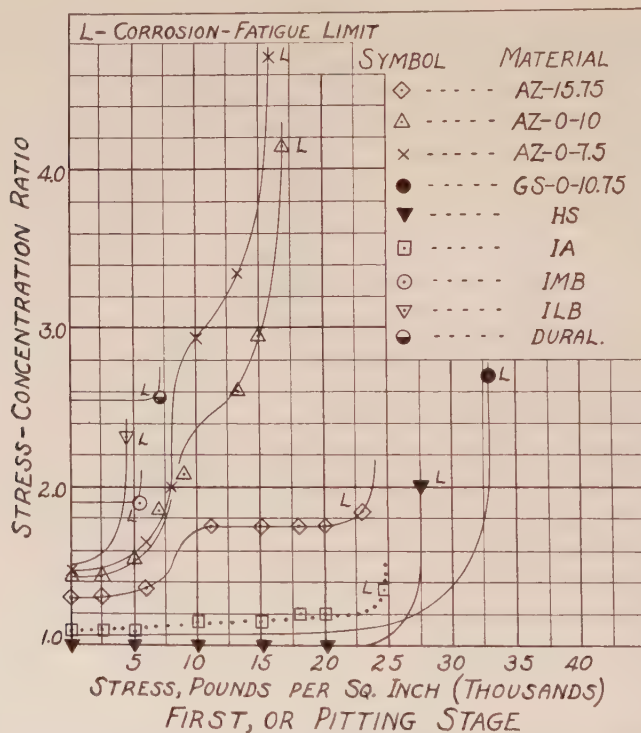


FIG. 3.—RELATION BETWEEN CYCLIC STRESS IN STAGE 1 AND STRESS CONCENTRATION DUE TO CORROSION PITTING, FOR VARIOUS METALS.

In Fig. 3, abscissas represent stage 1 stresses and ordinates represent stress-concentration ratios. The axis of abscissas represents the stress-concentration ratio (1.0) of uncorroded specimens. Although each graph in Fig. 3 resembles somewhat an inversion of the corresponding graph in Fig. 2, the proportions of the different parts of the graph in the two figures differ greatly. This is due to the fact that with decrease in the ordinate in Fig. 2 slight ordinate variations represent increasingly great variations in stress concentration. The graphs in Fig. 3, therefore, reveal some relationships that are not so clearly revealed in Fig. 2.

As indicated by the graphs for chrome-vanadium steel in Fig. 3, the stress concentration increases as the steel becomes harder. With increase in stage 1 stress, the stress concentration rises slowly at first. The rapidity of the rise increases, however, until at a stage 1 stress of about 8000 or 9000 for all three steels, the rate of increase of stress concentration is very great. With further increase of stage 1 stress the rate of increase of stress concentration slackens abruptly until the rate is small for quenched and tempered steel and is practically zero for the fully annealed steel. This reduced rate of increase of stress concentration continues until at a stage 1 stress near the corrosion-fatigue limit the stress concentration again begins to rise rapidly.

Possible Causes of Complexity of Graphs in Figs. 2 and 3

Depth Limitation of Notches.—The increase in stress concentration with increase in stage 1 stress to about 9000 would naturally be attributed to an increase in depth of corrosion pits. This conclusion is confirmed by visual examination, although such examination has not kept pace with the fatigue experiments. At a stage 1 stress of about 9000 or 10,000, the pits change abruptly from the round shallow form, which is found after stressless corrosion, and become sharp, relatively deep notches perpendicular to the direction of cyclic stress. This critical stage 1 stress therefore may be called the "notching stress" or "notching limit."

The observed slackening in the rate of increase of stress concentration with increase of stage 1 stress above the notching limit would naturally be attributed to a slackening in the rate of increase of notch depth. Such a tendency to depth limitation might be due to the increasing column of solid products of corrosion through which the corroding liquid must diffuse to reach the advancing edge of the notch. It seems probable that there is such a tendency to depth limitation and that the depth limit for any alloy depends on the character and adherence of the corrosion products.

For chrome-vanadium steel in contact with the fresh water used in these experiments the depth limit is evidently reached before (through stress concentration) the actual stress at the bottoms of the notches reaches the endurance limit. Failure, therefore, does not occur at the notching limit. To cause failure the nominal stress must be raised above the notching limit until the actual stress at the bottoms of the pits reaches the endurance limit. Under these conditions, therefore, the corrosion-fatigue limit is above the notching limit.

Influence of Calcium Carbonate on Depth Limit.—In discussing a previous paper³ by the author, Mr. Bayliss pointed out that from the carbonate water used in these experiments calcium carbonate is deposited on steel, and that this deposit has a decided protective effect. It seems possible, therefore, that the notch-depth limit for the chrome-vanadium

steels used in these experiments is less than it would be if a fresh water relatively free from carbonate had been used. Possibly in contact with water free from carbonate, the notch-depth limit would be great enough to permit the actual stress at the notching limit to reach the endurance limit. Under such conditions, the corrosion-fatigue limit and the notching limit would coincide.

As shown in a previous paper⁴ the corrosion-fatigue limit of a carbon steel in salt water is about 7000 or 8000. This limit is very near the notching limit for chrome-vanadium steel in contact with carbonate water. It seems possible, therefore, that for steel in contact with salt water the corrosion-fatigue limit is at the notching limit, whereas for steel in contact with carbonate water the corrosion-fatigue limit is considerably above the notching limit. This would explain the fact that for steels in contact with carbonate water the corrosion-fatigue limit is much higher than for steels in contact with salt water. The fact that for non-ferrous metals in contact with carbonate water the corrosion-fatigue limit is little if any higher than for these metals in contact with salt water, may be explained on the assumption that an adherent, protective carbonate film is not formed on non-ferrous metals.

Effect of Thickness of Specimens.—For thin specimens the intrinsic depth limit of notches would probably be little if any greater than for the relatively thick specimens used in the above described experiments. Owing to the effect of decreasing section of the specimen with increase in depth of notch, however, the rise of actual stress with increase in notch depth would be much greater for thin than for thick specimens. Hence it is possible that for thin sheet steel, even in contact with carbonate water, the depth limit would not be reached before the actual stress at the notching limit would reach the endurance limit. For thin sheet steel in contact with carbonate water, therefore, the corrosion-fatigue limit may be much lower than for thick specimens.

Effect of Repeated Stress on Metal at Bottom of Notch.—It seems possible that the form of the graphs in Figs. 2 and 3 may be somewhat influenced by the well known strengthening effect of repeated stresses slightly below the endurance limit. As pitting proceeds in a specimen subjected to nominal cyclic stress near the corrosion-fatigue limit the actual stress at the bottoms of the notches rises toward the endurance limit. The metal at the bottoms of the notches, therefore, is strengthened by repeated stress. Consequently, as stress concentration rises with progress of the notch, the endurance limit of the metal at the bottom of the notch tends to keep pace with the rise in stress concentration. The notch, therefore, has to advance further than it would in unchanged metal, before it reaches the endurance limit of the locally strengthened metal. The calculated stress-concentration ratio would thus be somewhat below the true value.

Whether the local strengthening of metal at the bottoms of the notches has appreciable effect on the form of the graphs in Figs. 2 and 3 cannot be decided definitely at present. It seems probable, however, that the effect is slight in comparison with the above described effect of notch-depth limitation.

*Elevation of Corrosion-fatigue Limit Due to Strengthening of Metal in Path of Corrosion Pit **

The corrosion-fatigue limit of a specimen may be elevated by local strengthening of metal in the path of each advancing notch. When the initial stress in a corrosion-fatigue test is below the endurance limit but above the corrosion-fatigue limit, the actual stress increases gradually on account of pitting, until at the bottom of each notch the stress reaches the endurance limit. The rapidity of the approach of the actual stress to the endurance limit decreases as the initial stress nears the corrosion-fatigue limit. At, or slightly above, the corrosion-fatigue limit, therefore, conditions are favorable for appreciable strengthening of metal at the bottoms of the advancing notches. For this reason the corrosion-fatigue limit may be higher than if there were no such local strengthening. Whether the elevation of the corrosion-fatigue limit from this cause is great or even appreciable cannot be decided at present.

PART III. EFFECT OF CYCLIC STRESS ON CORROSION OF CORROSION-RESISTANT STEEL

Medium-chromium, High-nickel Steel, Material HS

In Fig. 4a are shown ordinary fatigue and corrosion-fatigue graphs for a corrosion-resistant steel of the austenitic type. The corrosion-fatigue limit for this steel is higher than for carbon and ordinary alloy steels such as the chrome-vanadium steel described in Part II. The flatness of the endurance graph for this material is due to its low thermal conductivity. The influence of thermal conductivity on the form of the stress-cycle graph has been discussed in a previous paper.¹

Results of prior-corrosion fatigue tests of material HS are presented in Fig. 4b. To avoid obscuring these results the fatigue and corrosion-fatigue lines are repeated without the individual test results. Each small inverted triangle indicates by its position the result of a stage 2 test. Beside each triangle is a key letter, by means of which the stage 1 stress and number of cycles may be obtained from a list accompanying the figure. Zigzag lines in this figure have the same meaning as in Fig. 1.

The low result obtained with specimen *R*, shown by its position in Fig. 4b, indicates that this specimen was defective. As this specimen was one of the first tested, the low result was the cause of the unneces-

STAGE 1 STRESSES AND CYCLES

Fig. 4b			Fig. 5c		
Material HS			Material GS-0-10.75		
Symbol	Fresh Water		Symbol	Fresh Water	
	Stress, Lb. per Sq. In.	Cycles Millions		Stress, Lb. per Sq. In.	Cycles Millions
B	5,000	21.6	A	5,000	19.9
C	20,000	21.4	B	10,000	19.7
G	20,000	20.9	C	10,000	20.0
H	20,000	20.5	D	20,000	20.8
P	10,000	19.9	E	20,000	19.5
Q	10,000	21.2	F	23,000	19.7
R	15,000	20.2	G	25,000	20.2
T	30,000	19.7	H	30,000	20.0
U	25,000	19.9			
V	10,000	20.0			
W	15,000	20.0			

Fig. 6			Fig. 7		
Material IA			Material IU-8		
A	2,000	48.2	A	5,000	49.5
B	5,000	51.0	B	15,000	50.1
C	5,000	55.4	C	20,000	51.3
D	10,000	31.7	D	10,000	50.7
E	10,000	51.6	E	18,000	50.4
F	15,000	52.5	F	20,000	50.7
G	15,000	55.8			
H	18,000	64.3			
I	18,000	52.9			
J	20,000	31.0			
K	20,000	52.0			

Fig. 8b

Material ILB

A	2500	52.4
B	2500	49.6
C	4000	49.2
D	3000	49.2
E	3000	49.2

sarily low initial stress used with the following specimens *T* and *U*, and with several other specimens.

The results of the stage 2 tests shown in Fig. 4*b* indicate that with the exception of the defective specimen *R*, the fatigue limit of this material is practically unaffected by corrosion at stage 1 stresses up to 20,000. Three specimens tested at 25,000 and two specimens tested at 30,000,

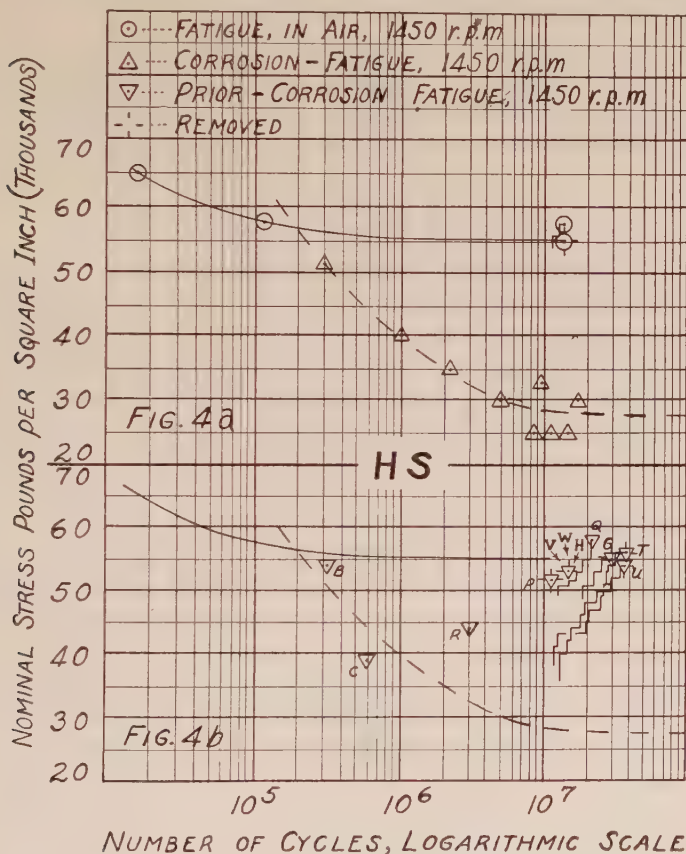


FIG. 4.—CORROSION OF MEDIUM-CHROMIUM, HIGH-NICKEL STEEL AS AFFECTED BY CYCLIC STRESS.

as shown in Fig. 4*a*, failed in the first stage. As shown in Fig. 4*b*, however, specimens *T* and *U*, tested at 25,000 and 30,000, respectively, did not fail until the stress in the second stage had been gradually raised to the endurance limit.

The relationship between stage 1 stress and stage 2 fatigue limit is illustrated by the graph for material HS in Fig. 2. The graph starts at a point representing the endurance limit of the material and extends to the

right at the same level until the abscissa is only slightly less than the corrosion-fatigue limit. The graph then descends almost vertically to the axis of ordinates.

The relationship between stage 1 stress and resulting stress concentration is illustrated by the graph for material HS in Fig. 3. As illustrated by this graph, the stress-concentration ratio remains about 1.0, while the stage 1 stress increases from zero almost to the corrosion-fatigue limit. The stress concentration then rises rapidly.

The results illustrated in Figs. 2 and 3, therefore, would seem to indicate that, for this corrosion-resistant steel, there is a fairly distinct stress limit below which pitting is negligible. This "pitting limit" evidently is not far below the corrosion-fatigue limit.

Stainless Steel, Material GS

In Fig. 5 are shown fatigue and corrosion-fatigue graphs for stainless steel that had been heat-treated in three different ways. Fig. 5a represents fully annealed material. Fig. 5b and Fig. 5c represent material that, after quenching, had been drawn at two different temperatures.

The solid-line graphs in Fig. 5 represent results of ordinary fatigue tests. As insufficient material was available to obtain a fatigue graph for the fully annealed material GS-17, the solid-line graph for this material in Fig. 5 was taken from the graph for similar material FJ-17 of a previous paper.² The fatigue limits as estimated from the three fatigue graphs in Fig. 5 are nearly in proportion to the tensile strength, although the limit for material GS-17 is slightly lower and the limit for material GS-0-12 is slightly higher than would be expected.

The corrosion-fatigue limits for materials GS-17 and GS-0-12 evidently differ little. The wide scatter of results of corrosion-fatigue tests for material GS-0-10.75 makes it difficult to decide on a corrosion-fatigue limit. Apparently, however, the average corrosion-fatigue limit for this hard material is somewhat lower than for the softer materials GS-17 and GS-0-12.

Results of prior-corrosion fatigue tests as well as the results of corrosion-fatigue tests for material GS-0-10.75 show wide scatter. It will be observed that for stage 1 stresses above about 25,000 the results are very erratic. Whereas two specimens failed in stage 1 under a stress of 30,000, and one at 27,000, other specimens *H* and *G* endured stage 1 stresses of 30,000 and 25,000, respectively, and in stage 2 showed a probable fatigue limit of about 77,000 and 74,000, respectively. Another specimen, tested at a stress of 40,000, practically completed stage 1 before failure. On account of the wide scatter of results, therefore, the tests were too few to establish definitely the positions of the stage 2 graphs. The graphs as drawn, however, are probably not far from their correct average positions.

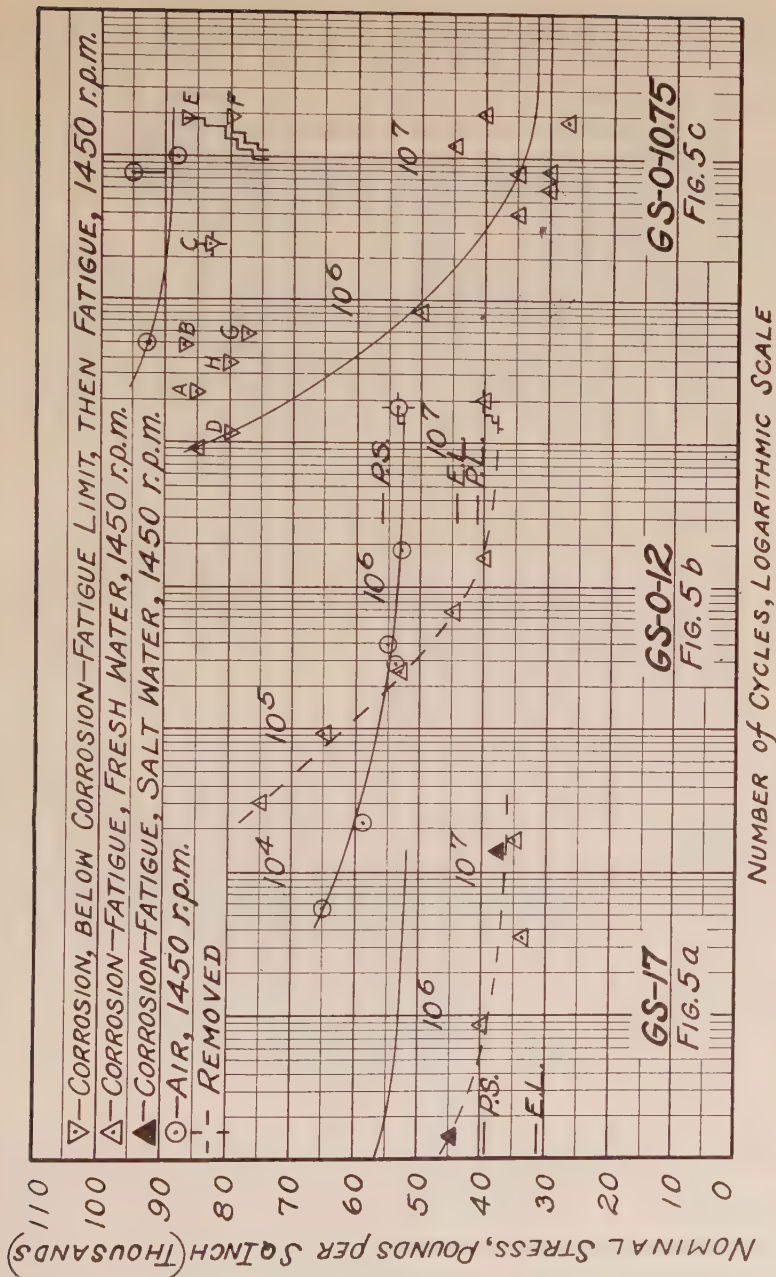


Fig. 5.—CORROSION OF STAINLESS STEEL AS AFFECTED BY CYCLIC STRESS.

By use of the data in Fig. 5c, graphs have been drawn in Figs. 2 and 3 to represent the approximate average relationship of the stage 1 stress to the stage 2 fatigue limit and stress concentration. As shown in Fig. 2, the graph for material GS-0-10.75 starts not far below the endurance limit *D*. The graph is at first nearly horizontal and the slope increases only slightly until the abscissa exceeds about 25,000. The slope then rapidly increases until beyond an abscissa of about 33,000 the graph becomes nearly vertical.

As indicated by the graph in Fig. 3, unless the stage 1 stress exceeds 20,000 to 25,000 the resulting stress concentration is low, in spite of the great hardness of this material. This indicates that at stage 1 stresses below a fairly definite limit, pitting is very slight. This conclusion is confirmed by visual examination. Below the pitting limit few pits are visible. They are apparently shallow, and visible only with the microscope.

Comparison of Behavior of Two Types of Steel

The results presented in Parts II and III are evidently typical of the behavior of two kinds of steel. Carbon and ordinary alloy steels are severely pitted even when the corrosion is at zero stress. The depth and sharpness of the pitting increases greatly with increase in the cyclic stress. Corrosion-resistant steels are not severely pitted by corrosion at zero stress, or at any stress below a fairly definite pitting limit, which practically coincides with the corrosion-fatigue limit. Whether this difference of behavior between the two types is due largely to physical properties of the surface film will be considered later. Evidence to be presented in Parts IV and V, however, seems to indicate that the former type of behavior is characteristic of high-potential (high solution pressure) alloys and the latter type is characteristic of low-potential alloys.

PART IV. EFFECT OF CYCLIC STRESS ON CORROSION OF ALLOYS OF COPPER AND OF NICKEL

Aluminum Bronze

In Fig. 6 are shown results of prior-corrosion fatigue tests of aluminum bronze. Results of fatigue and corrosion-fatigue tests of this material were presented in a previous paper.⁴ The same paper also presented results of stressless corrosion followed by fatigue. For this reason, and also to avoid confusion, individual results of tests of these three types are not given in Fig. 6. The stress-cycle relationship, however, for the three types of test is represented by the lines *A*, *B* and *C* in the upper set of graphs in Fig. 6.

In the lower three sets of graphs of Fig. 6 are shown results of stage 2 tests of specimens that in stage 1 had been subjected to various stresses between zero and the corrosion-fatigue limit. The method of representing the individual results is the same as that used in Figs. 1 and 4.

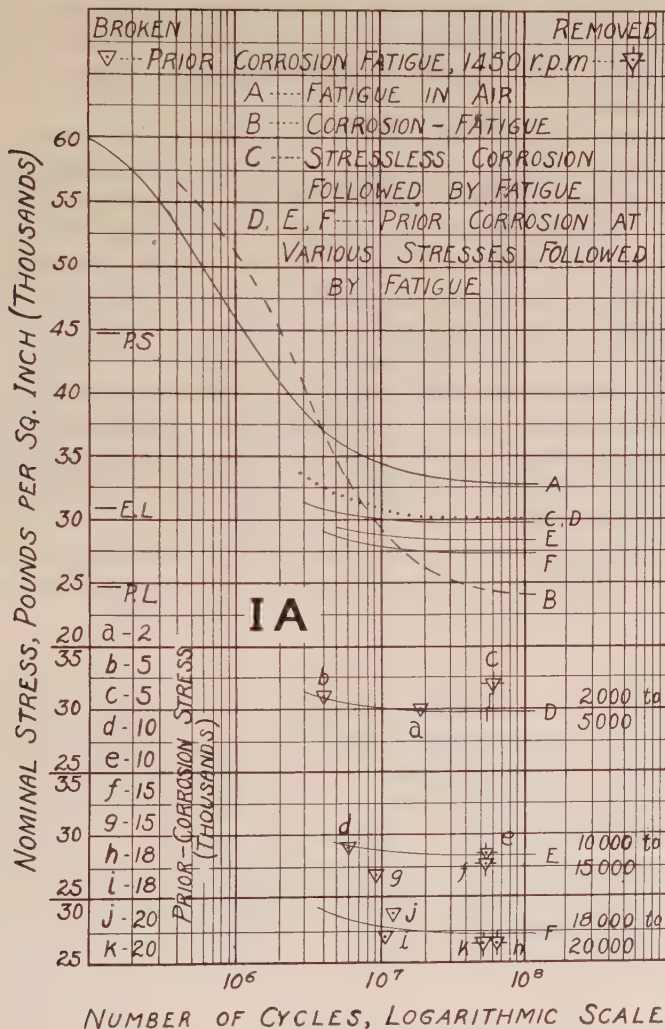


FIG. 6.—CORROSION OF ALUMINUM BRONZE AS AFFECTED BY CYCLIC STRESS.

The light solid lines in the lower three spaces of Fig. 6 have been drawn to represent approximately the stage 2 relationship that seems to be in accordance with the individual tests. The numbers at the right of each line indicate the corresponding stage 1 stresses. In spite of rather wide scatter of individual result, it is believed that the relative positions in the lower three spaces of Fig. 6 are approximately correct.

In the upper space of Fig. 6 have been assembled all the lines representing fatigue, corrosion-fatigue and prior-corrosion fatigue. As illustrated by lines *C* to *F*, the position of the stage 2 graph is practically unaffected by increase in the stage 1 stress from zero to 5000. With increase in the stage 1 stress from 5000 to 20,000, the stage 2 graph descends appreciably. With further increase in stage 1 stress from 20,000 to the corrosion fatigue limit (24,000) the descent of the stage 2 graph is much greater.

The relationship between stage 1 stress and stage 2 fatigue limit is illustrated by the dotted-line graph in Fig. 2. This graph starts only slightly below the point *F* representing the endurance limit. As it extends to the right, the graph, at first practically horizontal, curves downward only slightly before it reaches an abscissa of about 20,000. The slope then gradually increases until at the point *L*, representing the corrosion-fatigue limit, the graph becomes nearly vertical.

This graph and the corresponding stress-concentration graph in Fig. 3 resemble the graphs for corrosion-resistant steels more than they resemble the graphs for chrome-vanadium steels. For aluminum bronze, as for corrosion-resistant steels, corrosion pitting is evidently not severe at cyclic stresses below a fairly definite limit, which is not far below the corrosion-fatigue limit.

It is worthy of note that the electrolytic potential of this alloy is nearer to the potential of corrosion-resistant steel than to the potential of chrome-vanadium steel.

Nickel-copper Alloys

In Fig. 7 are shown fatigue and corrosion-fatigue graphs for copper and for some of its alloys with nickel. The graphs are arranged from left to right in order of increasing nickel content. The two graphs at the left represent cold-rolled and hot-rolled copper. The adjacent graph represents a cold-rolled alloy containing about 2.5 per cent. nickel. The next pair of graphs represent cupronickel containing about 21 per cent. nickel. The set of graphs on the extreme right represent monel metal. As the graphs for copper and cupronickel have been previously published^{3,4} results of individual tests are omitted, and only the stress-cycle lines are shown.

It was shown in previous papers^{3,4} that the corrosion-fatigue limit, for nickel-copper alloys having about 21 to 99 per cent. nickel, varies only slightly with composition or mechanical working. It was also shown that, for nickel-copper alloys having less than about 21 per cent. nickel, the corrosion-fatigue limit is not below the endurance limit. It was surmised that for these alloys the intrinsic corrosion-fatigue limit is above the endurance limit. Each of the nickel-copper alloys represented in Fig. 7 will now be considered separately.

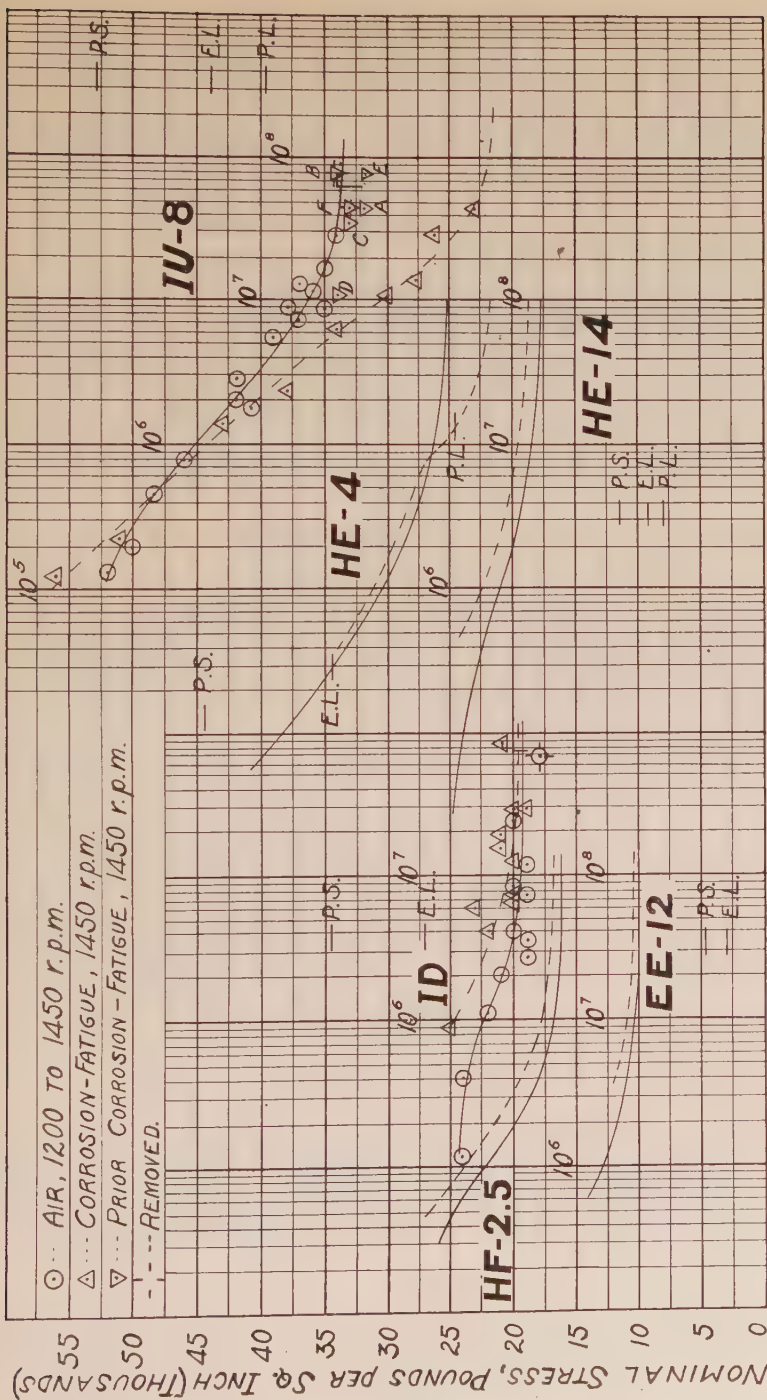


FIG. 7.—CORROSION OF COPPER AND SOME COPPER-NICKEL ALLOYS AS AFFECTED BY CYCLIC STRESS.

Monel Metal

Results of fatigue, corrosion-fatigue and prior-corrosion fatigue tests of monel metal are represented in Fig. 7 in the usual way. The lower portion of the fatigue graph as usual is a curve descending toward a horizontal asymptote. As mentioned in a previous paper⁴ the corrosion-fatigue limit for monel metal is practically the same as for cupronickel, material HE-4, although the two alloys differ greatly in chemical composition and physical properties.

Results of prior-corrosion fatigue tests, as shown in Fig. 7, indicate that the stage 2 fatigue limit is affected very little by prior-corrosion at stresses below the corrosion-fatigue limit. For this low-potential alloy, as for the corrosion-resistant steel HS, pitting is negligible at cyclic stresses below a fairly definite pitting limit which practically coincides with the corrosion-fatigue limit.

Cupronickel

As illustrated by the graphs for cupronickel in Fig. 7, the corrosion-fatigue limit of the fully annealed material, HE-14, is not below the endurance limit. For the cold-worked material HE-4, the corrosion-fatigue limit is below the endurance limit, but above the endurance limit of the fully annealed material. As stated in previous papers,^{3,4} this relationship seems to indicate that for fully annealed cupronickel the intrinsic corrosion-fatigue limit is above the endurance limit, and that the intrinsic corrosion-fatigue limit is not encountered unless this material is strengthened by cold working.

In the light of the above described behavior of monel metal and other low potential alloys, this behavior of cupronickel is not surprising. For the fully annealed material HE-14 there is evidently no appreciable corrosion-pitting at cyclic stresses below the endurance limit. The pitting limit (which is the above mentioned "intrinsic corrosion-fatigue limit") is above the endurance limit. For the cold-worked material, the corrosion-fatigue limit is probably the pitting limit.

2.5 Per Cent. Nickel Alloy

As shown by the graphs for material ID in Fig. 7, the corrosion-fatigue limit of this cold-worked alloy is not below the endurance limit. Evidently, for this alloy as for the fully annealed cupronickel, the pitting limit, or intrinsic corrosion-fatigue limit, is above the endurance limit.

Copper

As shown by the graphs for copper in Fig. 7 the corrosion-fatigue limit, even for severely cold-worked material, is not below the endurance limit. Although this metal becomes heavily coated by corrosion, its fatigue

resistance is not lowered. And yet as mentioned by H. F. Moore,⁸ notches and other abrupt changes of section greatly influence the fatigue resistance of this metal. For copper, therefore, as for the low-potential alloys described above, there is evidently a definite pitting limit, below which there is no important pitting. This pitting limit is not encountered, even in the severely cold-worked metal represented in Fig. 7.

Muntz Metal

A few prior-corrosion fatigue experiments have been made with Muntz metal. Though not enough experiments have been made to justify the drawing of graphs, the results indicate that this alloy behaves more like the chrome-vanadium steel than like the copper-nickel alloys or the corrosion-resistant steels. The fatigue limit is considerably lowered by stressless corrosion, especially in salt water. It is worthy of note that the potential for this alloy is higher than for any of the alloys described thus far in this paper except the chrome-vanadium steel.

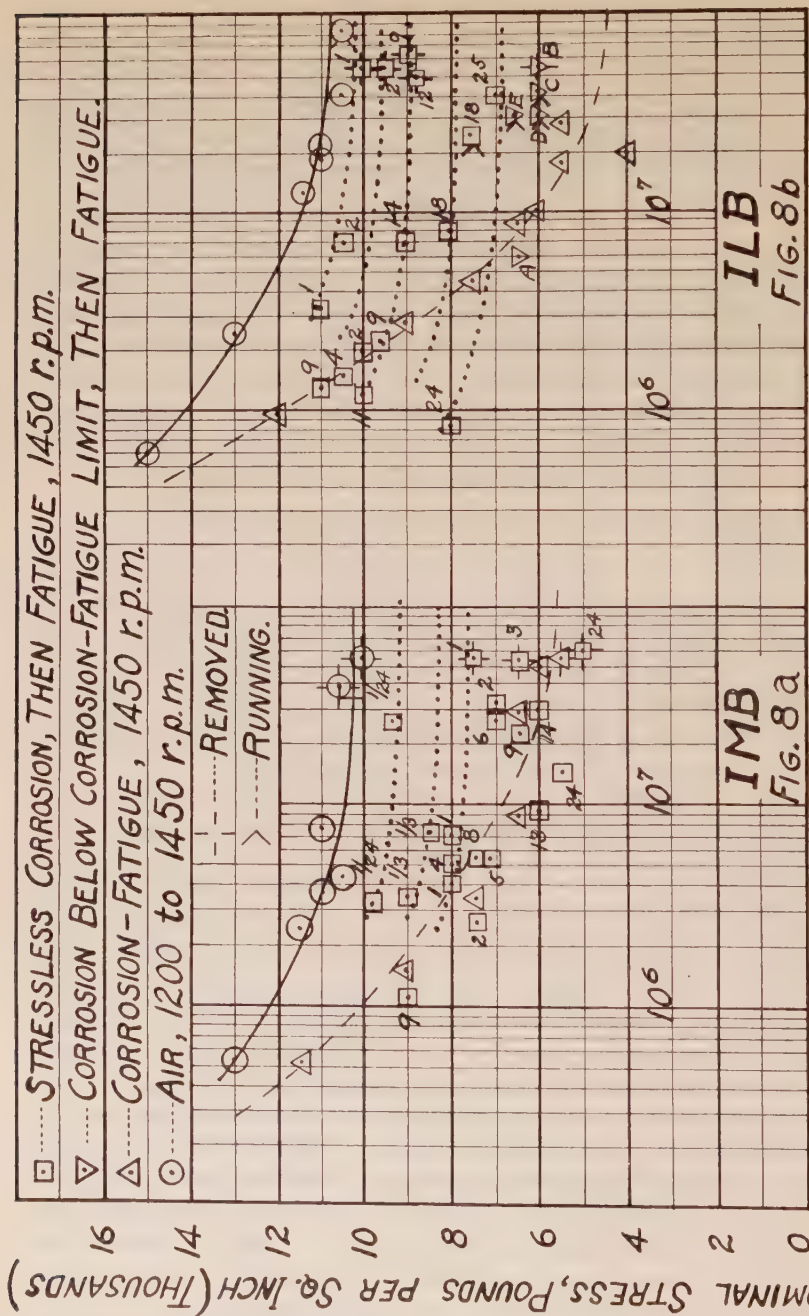
PART V. EFFECT OF CYCLIC STRESS ON CORROSION OF ALUMINUM ALLOYS

Commercial Aluminum

The effect of stressless corrosion on commercial aluminum that had been cold worked to "hard" temper, is illustrated by the small squares in Fig. 8a. The small numeral beside each square indicates the number of days' stressless corrosion. The position of each square shows the effect of corrosion on the fatigue resistance. Results of fatigue and corrosion-fatigue tests are also included in this figure.

The damaging effect of stressless corrosion on commercial aluminum is remarkably great. One hour's corrosion lowers the fatigue limit appreciably; 8 hr. corrosion lowers the fatigue limit by nearly half; one day's corrosion lowers it by more than half; and two days' corrosion lowers it about three-fourths the difference between the endurance limit and the corrosion-fatigue limit. With increase in prior-corrosion time from 2 to 9 days, the fatigue graph descends by gradually decreasing steps until it is practically at the corrosion-fatigue limit. With further increase in corrosion-time from 9 to 25 days the fatigue graph apparently descends slightly below the corrosion-fatigue graph. Possibly the corrosion conditions were slightly more severe in stressless corrosion than in corrosion-fatigue. The logical conclusion from the results presented in Fig. 8a is that for commercial aluminum stressless corrosion for more than a day or two lowers the fatigue resistance about as much as if the material at the same time had been stressed at the corrosion-fatigue limit. Cyclic stress below the corrosion-fatigue limit, therefore, has little influence on corrosion pitting of commercial aluminum.

⁸ H. F. Moore and S. W. Lyon: Tests of the Endurance of Gray Cast Iron under Repeated Stress. *Proc. Am. Soc. Test. Mat.* (1927) Pt. II, 27.



Aluminum-manganese Alloy

The aluminum-manganese alloy had been cold worked to "hard" temper. In Fig. 8b are shown results of stressless corrosion followed by fatigue in air. Results of fatigue and corrosion-fatigue tests are also included.

As shown in the figure, stressless corrosion for only one or two days lowers the fatigue resistance appreciably. With increase in the prior corrosion time, the fatigue graph descends by gradually decreasing steps. As the corrosion-fatigue graph at 50,000,000 cycles (25 days) is nearly horizontal, increase of stressless corrosion time beyond about 25 days would probably affect the fatigue resistance very little. The fatigue resistance is damaged less by stressless corrosion for 25 days than by simultaneous corrosion and stress at the corrosion-fatigue limit. In this respect the aluminum-manganese alloy differs from commercial aluminum.

A few experiments have been made with stage 1 stresses below the corrosion-fatigue limit. The results as shown in Fig. 8 are about midway between the results of 25 days' stressless corrosion and the results of corrosion-fatigue. The effects of stressless corrosion of this material are so great and the corrosion-fatigue limit is so low that further investigation of the effect of stress below the corrosion-fatigue limit seems undesirable.

Duralumin

Results presented in a previous paper⁴ indicate that for duralumin, the effect of stressless corrosion for 10 days or more is nearly as great as if the material at the same time had been stressed at its corrosion-fatigue limit. These conclusions are confirmed by recent results not presented here in detail. For all samples of duralumin investigated, cyclic stress below the corrosion-fatigue limit had little influence on corrosion. In this respect, therefore, duralumin resembles commercial aluminum more than it resembles the aluminum-manganese alloy.

Summary for Aluminum Alloys

In Figs. 2 and 3 are graphs illustrating the relation of stage 1 stress to stage 2 fatigue limit or to stress concentration, for aluminum, aluminum-manganese alloy, and duralumin. As shown in these figures the graphs for aluminum-manganese alloy differ considerably in form from the graphs for the other two alloys. The graphs for aluminum-manganese alloy curve considerably between the origin and the point *L* representing the corrosion-fatigue limit. Between these two points the graphs for aluminum-manganese alloy have been drawn on the assumption that

from the origin to the point *L* they are simple curves, and that for this alloy the corrosion-fatigue limit corresponds to a "notching limit."

The difference in form between the graph for aluminum-manganese alloy and the graphs for the other two aluminum alloys is especially conspicuous in Fig. 3. The relatively high origins of the graphs for aluminum and duralumin are evidence of the severity of the pitting at zero stress. The pitting is so severe that even at zero stress there is depth limitation. This explains the fact that increase of stress from zero to the corrosion-fatigue limit has practically no influence on pitting. The reason for the lack of slope of the graphs for aluminum and duralumin, therefore, is the same as the reason for the lack of slope of the corresponding portion of the graph for fully annealed steel, AZ-15.75. This reason has been discussed fully in Part II.

For the aluminum-manganese alloy, on account of its higher corrosion-resistance, the pits at zero stress are shallower than for the other two alloys, and with increase of stress from zero to the corrosion-fatigue limit there is no evidence of notch depth limitation. For aluminum of high purity it is reported that corrosion at zero stress is much less severe than for the commercial aluminum used in these experiments. A graph for aluminum of high purity, therefore, would probably resemble in form the graph in Fig. 3 for aluminum-manganese alloy. Whether the notching limit for pure aluminum is higher than that for the aluminum-manganese alloy has yet to be determined.

PART VI. INFLUENCE OF ELECTROCHEMICAL AND PHYSICAL PROPERTIES ON BEHAVIOR OF ALLOYS UNDER CORROSION AND CYCLIC STRESS

In Fig. 2 the relative position of the origin of each graph depends not only on the electrochemical, but also on the physical properties of the alloy. The origin of the graph for the hard material GS-0-10.75, for example, is considerably above the origin of the graph for the softer material HS, although the two alloys differ little in electrolytic potential.

In Fig. 3 the graphs from lowest to highest are located in order of increasing electrolytic potential. Stress concentration, therefore, tends to be greater the higher the potential of the alloy. Stress concentration, however, depends not only on electrolytic potential but also somewhat on physical properties. For this reason the graph for the hardest chrome-vanadium steel in Fig. 3 is uppermost, and the graph for the softest is lowest, of the three graphs for steel. For the same reason the graph for duralumin is higher than the graph for the softer commercial aluminum.

The corrosion-fatigue limits of the various alloys represented in Figs. 2 and 3, taken as groups, are in the order of their electrolytic potentials. Aluminum alloys, the group having highest potential, have the lowest corrosion-fatigue limits; corrosion-resistant steels, the alloys of lowest

potential, have the highest corrosion-fatigue limits. Nevertheless there are irregularities in the quantitative relationship of electrolytic potential to corrosion-fatigue limit. The corrosion-fatigue limit for the fully annealed steel, AZ-15.75, for example, is nearly equal to that of the alloy IA, whose potential is much lower. The corrosion-fatigue limit for duralumin also is greater than would be accounted for by its potential. These and other irregularities are apparent if potentials of alloys in fresh water be plotted as ordinates with corrosion-fatigue limits as abscissas.

In a previous paper⁴ it was shown that if potentials of alloys in salt water be plotted as ordinates, with corrosion-fatigue limits as abscissas, most of the resulting points are not far from a fairly smooth curve. Nevertheless there are irregularities in the positions representing some of the alloys. The results presented in the present paper indicate that these anomalies are due to notch-depth limitation. If "notching limits" instead of corrosion-fatigue limits be plotted as abscissas, with electrolytic potentials as ordinates, the results would probably form a fairly regular curve. The notching limit probably depends chiefly on electrochemical properties and is little influenced by physical properties.

Although no evidence of a notch-depth limit for any low-potential alloy has as yet been found, it may yet be found, possibly among the corrosion-resistant steels. On account of the relatively deep pitting of high potential alloys at low stresses, however, notch-depth limitation is probably more common in high-potential than in low-potential alloys.

The corrosion-fatigue limit for a low potential alloy is usually not far from the pitting limit. Under such conditions the influence of physical properties on the corrosion-fatigue limit is probably slight. The corrosion-fatigue limit for low potential alloys, therefore, is usually less dependent on physical properties than is the corrosion-fatigue limit for high-potential alloys.

An investigation of the effect of size of section on the corrosion-fatigue limit is much needed. Discussion of this subject at present must be merely tentative. The possible effect of thinning the section on the corrosion-fatigue limit of steel was discussed briefly in Part II. With decrease of specimen section from a relatively large value to a thickness of only once or twice the depth of stressless corrosion pits, the corrosion-fatigue limit would evidently decrease to zero. The rate of decrease in corrosion-fatigue limit would obviously increase as the thickness is decreased. How thin the section can become without affecting the corrosion-fatigue limit seriously would depend on the type of alloy. For alloys that can be severely pitted at zero stress, and especially for alloys that (in the form of relatively large specimens) show notch-depth limitation at low stresses, the effect of thinning section on the corrosion-fatigue limit would be relatively great. For low-potential alloys the effect of thinning section would be relatively small.

PART VII. EFFECT OF TIME AND NUMBER OF CYCLES ON CORROSION

In studying the effect of cyclic stress on corrosion, there are three factors to be considered: stress, time, and number of cycles. The effect

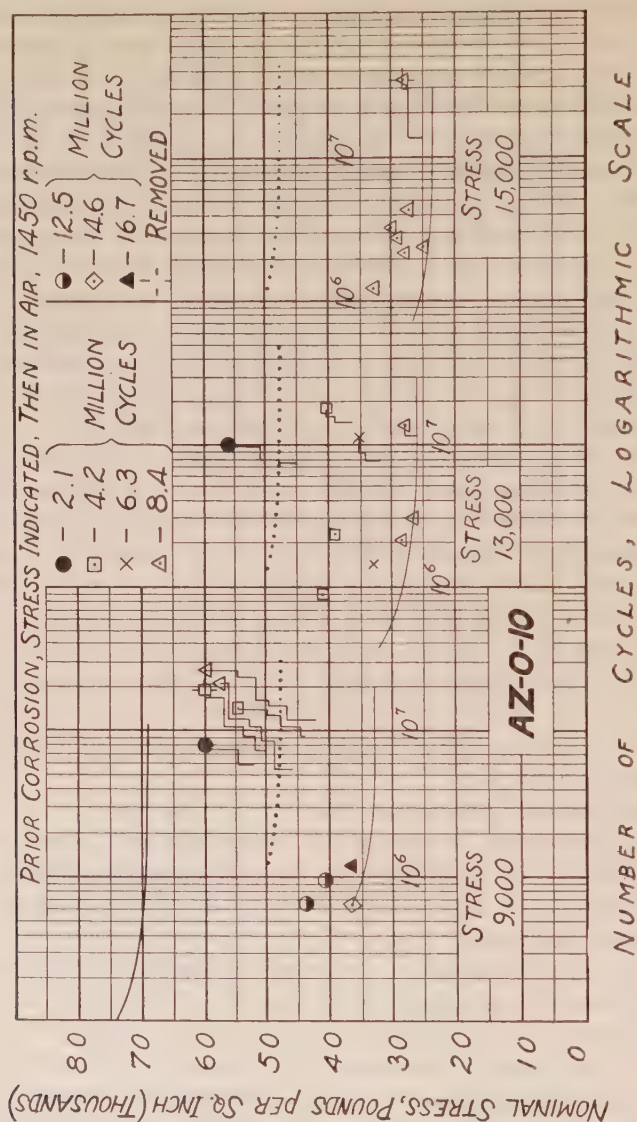


FIG. 9.—EFFECT OF VARYING NUMBER OF CYCLES WITH CONSTANT CYCLE FREQUENCY.

of stress has been discussed in Parts II to VI. The effect of time and number of cycles must now be considered.

The time factor may be expressed either as time per cycle or as total time. There are some advantages, however, in first presenting the results

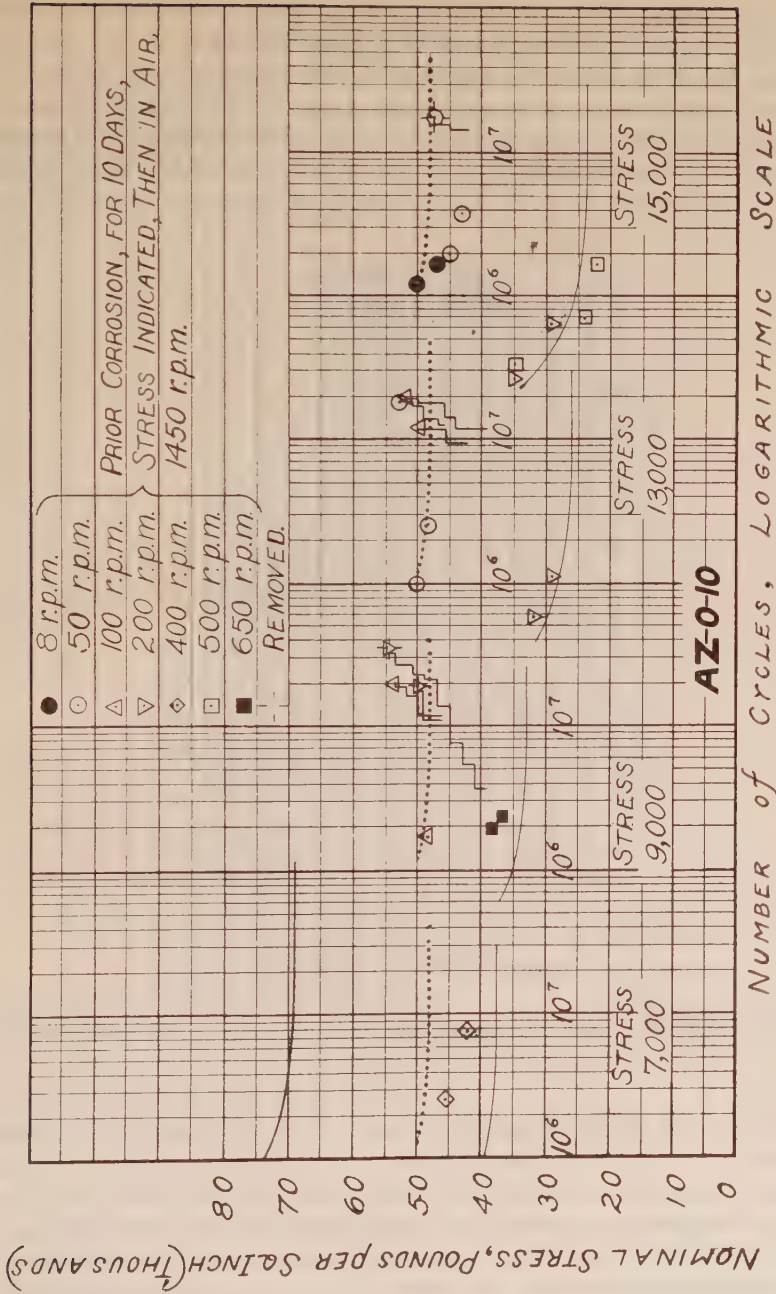


FIG. 10.—EFFECT OF VARYING CYCLE FREQUENCY WITH CONSTANT TOTAL TIME.

of the investigation in terms of cycle frequency and total number of cycles. The results are so presented in Figs. 9 to 12.

Figs. 9 and 11 illustrate the effect of varying number of cycles with constant cycle frequency (constant time per cycle). Figs. 10 and 12 illustrate the effect of varying cycle frequency (and varying total number of cycles) with constant total time. The material used in these experi-

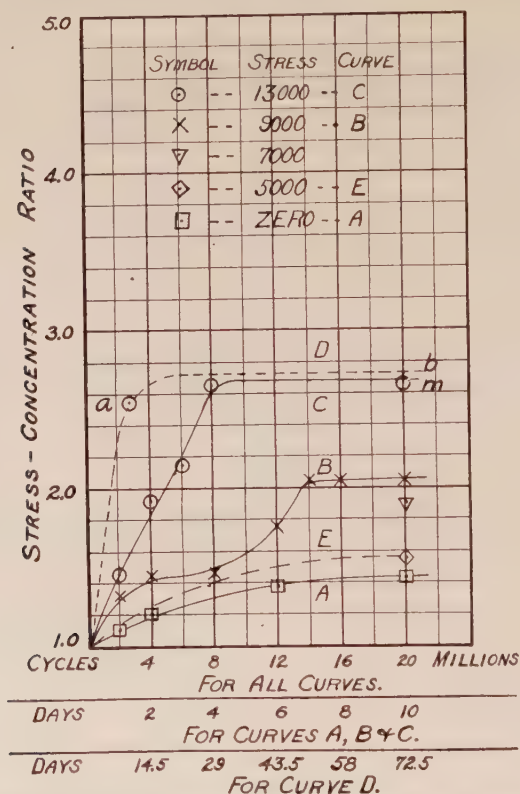


FIG. 11.—EFFECT OF VARYING NUMBER OF CYCLES AND TOTAL TIME, WITH CONSTANT CYCLE FREQUENCY.

ments was the chrome-vanadium steel, AZ-0-10, that was discussed in Part II.

Each stress-cycle graph in Figs. 9 and 10 represents results of fatigue tests after corrosion under definite conditions of stress, cycle frequency, and number of cycles. To supplement these results some stress-cycle lines, without the experimental points, have been transferred to Figs. 9 and 10 from Fig. 1. The lower solid lines in these figures represent the effect of corrosion at 1450 r. p. m. The dotted lines represent the effect of stressless corrosion. The upper solid lines are ordinary fatigue graphs.

Fatigue limits, estimated from the stress-cycle graphs in Figs. 9 to 10, have been utilized in calculating stress-concentration ratios, and these ratios have been plotted as ordinates against various abscissas in Figs. 11 and 12.

In Fig. 11, graphs *B*, *C* and *E* represent the effect of varying number of cycles (and varying total time) with constant cyclic stress and constant cycle frequency (1450 per min.). For comparison, graph *A* has

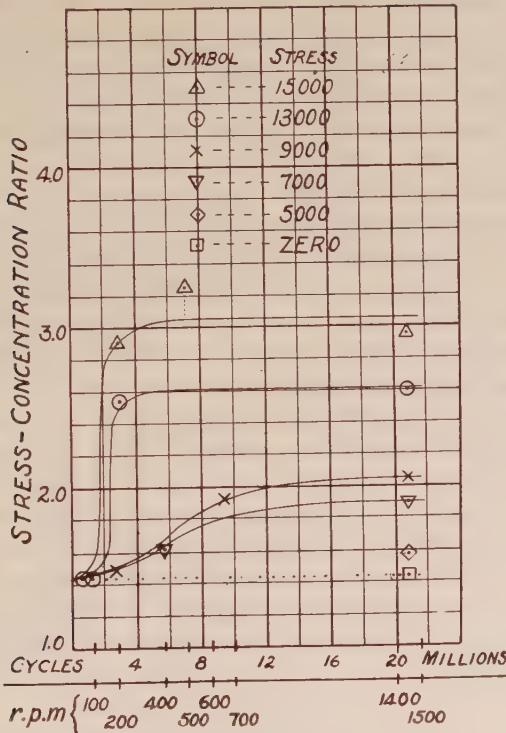


FIG. 12.—EFFECT OF VARYING CYCLE FREQUENCY AND TOTAL NUMBER OF CYCLES, WITH CONSTANT TOTAL TIME.

been plotted to represent the results of stressless corrosion. The time scale for graph *A* is the same as for graphs *B* and *C*.

Graph *A* is a simple curve approaching a horizontal asymptote, thus indicating that the depth of pitting at zero stress tends to approach a limit.

Graph *B* is of complex form somewhat resembling the graphs for chrome-vanadium steels in Fig. 3. Whether the upward convexity in the lower portion of this graph represents true relationship is not yet certain. It seems possible, however, that the lower portion of graph *B* represents

the formation of relatively shallow pits similar to the pits formed by stressless corrosion. The portion of graph *B* with upward curvature possibly represents the formation of a sharp notch at the bottom of the shallow pit. The horizontal portion represents depth limitation. Graph *C* shows a similar form, but the reversal of curvature in the sloping portion is less conspicuous.

As shown in Fig. 3, a stress of 13,000 for this material is above the "notching limit" and a stress of 9000 is not far from the notching limit. For stresses below the notching limit, graphs in Fig. 11 would probably be of simple form similar to graph *A*. Graph *E*, representing a stress of 5000, has been so drawn. The position of the right end of this graph has been estimated from data in Fig. 1. The form of this graph indicates that at this stress the corrosion pits are relatively shallow, similar to those formed by stressless corrosion.

Fig. 12 illustrates the effect of varying cycle frequency (time per cycle) and varying number of cycles, with constant total time (10 days). The graphs in Fig. 12 are similar in form to those in Fig. 11. They differ however, from the graphs in Fig. 11 in two respects: (1) The graphs in Fig. 12 start from a point representing the effect of ten days' stressless corrosion, whereas the graphs in Fig. 11 start from a point representing absence of corrosion; (2) the upper point of reversal of curvature (depth limitation) for a graph in Fig. 12 is reached at fewer cycles than is the similar point on the corresponding graph of Fig. 11. This is due to the fact that in Fig. 12 each point on a graph represents the effect of 10 days' total corrosion time, whereas each graph in Fig. 11 represents the effect of varying corrosion time as well as varying number of cycles.

Graph *D* in Fig. 11 has been drawn to represent the effect of cycle frequency 200 with varying number of cycles and total time. To obtain this graph, the point *a* has been transferred from Fig. 12 to Fig. 11. To the right of the point *a* in Fig. 11 the graph has been drawn on the assumption that it should be very little higher than graph *C*. This assumption appears justifiable in view of the fact that graph *C* extends to the right to the point *m* representing 20,000,000 cycles and 10 days. Increasing both number of cycles and total time much beyond these values, as is shown by many corrosion-fatigue graphs for steel, lowers the corrosion-fatigue graph very little. Hence the sevenfold increase of total time without increase in total number of cycles should raise the point *b* in Fig. 11 only slightly above the point *m*.

These conclusions are confirmed by corrosion-fatigue tests of steel (not illustrated here in detail) at 50 r. p. m. These tests indicate that the corrosion-fatigue limit at 50 r. p. m. differs very little from the limit obtained at 1450 r. p. m. At either of these two widely different cycle frequencies the corrosion-fatigue graph becomes nearly horizontal at four or five million cycles.

As represented by graphs *C* and *D* in Fig. 11, therefore, change in cycle frequency does not greatly affect the position of the horizontal portion of the graph, but affects considerably the number of cycles at which the sloping portion of the graph meets the horizontal portion.

The results presented in Figs. 11 and 12, therefore, indicate that depth of pitting or notching depends chiefly on the stress, provided the number of cycles exceeds a definite minimum which depends on the time per cycle. Time and number of cycles, provided they exceed a definite minimum, have little effect on depth of pitting. The minimum time and number of cycles necessary to reach the depth limit are interdependent. In further discussion, the number of cycles necessary to encounter notch-depth limitation will be called the "critical number of cycles" and the corresponding total time will be called the "critical time."

As illustrated by graphs *C* and *D* in Fig. 11, with increase in time per cycle the critical number of cycles decreases and the critical time increases. As indicated by the above-mentioned experiments, the critical number of cycles at 50 r. p. m. is probably little less than at 200 r. p. m. Hence it seems probable that with increase in time per cycle the critical number of cycles approaches a minimum.

Similar reasoning would indicate that with decrease in time per cycle the critical number of cycles would tend to become nearly inversely proportional to the time per cycle (proportional to cycle frequency). It seems not improbable, therefore, that at very high frequency, the critical time would tend to approach a minimum.

As illustrated by Fig. 12, specimens tested for 10 days at 8 or 50 r. p. m. showed little greater stress concentration than specimens subjected for the same length of time to stressless corrosion. When the cycles are few, the effect of stress below the corrosion-fatigue limit on corrosion of steel is negligible. The effect of a steady stress equal to the stress range used in these experiments (26,000) should also be negligible.

ACKNOWLEDGMENTS

Acknowledgment is due to the following personnel of the Naval Engineering Experiment Station: Capt. H. C. Dinger, U. S. N., Officer in Charge, and Lieut. Comdr. T. A. Solberg, U. S. N., Test Officer, for encouragement received in this investigation; Messrs. George F. Wohlgemuth, Associate Metallurgist; Laurence Thompson, Associate Metallurgist; M. C. Stewart, Assistant Metallurgist; W. E. Harvey, Junior Metallurgist, and John K. Amoss, Leadingman-machinist for assistance in the experiments.

Acknowledgment is also due to the following manufacturers: The International Nickel Co., the Aluminum Co. of America, the American Brass Co., the Firth-Stirling Steel Co., the Universal Steel Co., and the Alcumite Corp., for generously furnishing material.

DISCUSSION

H. S. RAWDON, Washington, D. C. (written discussion).—The author, in previous papers, has definitely shown that the endurance limit of metals under "fatigue" stresses is, in the great majority of cases, much lower if the metal is simultaneously subjected to a slight corrosive attack than if no corrosion occurs; also, that the effect of simultaneous corrosion and fatigue is very considerably greater than the effect produced by roughening the surface by a similar corrosive attack prior to stressing in fatigue. The general effect, in the latter case, of lowering the endurance limit might be predicted on the basis of our general knowledge of the effect of surface finish of test specimens upon the results of endurance testing. The aspect of the general problem presented in the present paper is somewhat novel, however; that is, the evaluation of the corrosive attack of a metal by subsequently subjecting the corroded specimens to an endurance test.

The points which the writer wishes to raise in this discussion bear on the more theoretical aspects of the explanation put forward by the author rather than on the practical application of the method to the general corrosion problem. It would seem that much more information must be accumulated before the really "practical" aspects of the problem can be discussed to any advantage.

The author has shown that "stressless corrosion" of specimens followed by endurance testing, in the absence of a corrodant, produces a lowering of the endurance limit, although the effect is not so pronounced as when the preliminary corrosive attack is accompanied by fatigue stressing. In a number of cases, a relatively slight initial corrosive attack ("stressless" corrosion, 1 hr. in the case of aluminum, Fig. 8a; 8 hr. for quenched and tempered Cr-V steel, Fig. 1c; and 1 day in most of the other cases) produced a much more pronounced effect relatively, when the specimen was subsequently fatigued, than did a more prolonged initial corrosive attack. In other words, the effect of prior corrosion ("stressless") upon the results of subsequent endurance tests is not additive although, for the conditions used (immersion in water which was constantly renewed) there is very good reason to believe that the severity of the corrosive attack at least, as ordinarily measured, is directly proportional to the length of the corrosion period. The author's conclusion (page 579) that "beyond about 10 days, the effect of increase in corrosion time is evidently slight" can hardly be taken to mean that, in general, corrosion of a Cr-V steel under the conditions given is one of gradually diminishing intensity.

The question has arisen in the writer's mind as to how much of the effect of "stressless" corrosion prior to fatigue may be attributed to the character of the initial surface finish of the test specimen. It is a matter of common knowledge in the microscopic study of metals that an apparently perfectly polished surface may be produced on a metal without removing all evidence of cold work (grinding and machining marks, scratches and the like). Slight etching serves to reveal them by removing the obscuring film of flowed metal on the surface which resulted from "forced" polishing. Granted that such a condition obtains on the surface of a specimen to be used for an endurance test, it would not be at all surprising that a slight initial etching (corrosion) which served to reveal the most pronounced of these hidden surface markings should produce a relatively greater effect than longer etching periods (prior to fatigue), nor that the effect, in general, should be one of gradual decreasing intensity. Tests of specimens, treated so as to remove as completely as possible all surface working effects, possibly by annealing the polished specimens in hydrogen, would be expected to throw some light on this point.

A rather careful study of the structural features of specimens which have corroded under the conditions used in this paper would also seem to be decidedly worth while. Corrosion often manifests itself in a variety of different forms and under various

disguises. It is hardly fair, for example, to consider the behavior, under corrosion, of an alloy such as Muntz metal in which the corrosive attack is usually confined practically entirely to one of the two constituents of this binary alloy, as being comparable with the corrosion of a simple metal, for example. The general subject of the effect of stress acting simultaneously with corrosion has previously received considerable attention from metallurgists and the conclusion seems to be warranted that often the corrosive attack of many metals and alloys under such conditions bears a rather definite and characteristic relationship to the structure of the material, the attack being of the intercrystalline type. In the opinion of the writer, the fact should be definitely established whether or not there is any tendency shown by any of the materials used, to be corroded in an intercrystalline manner when given the preliminary corrosive attack accompanied by fatigue. In order to determine this, it would undoubtedly be necessary to sacrifice a few specimens since a surface examination of the corroded bar would not suffice. Specimens after being corroded under stress should be sectioned and properly prepared so that microscopic examination at relatively high magnification up to the extreme edge of the section could be made. The observation of the author that with increase of stress the character of the corrosion pits changed and at a stress of 9000 to 10,000 assumed the form of "sharp relatively deep notches perpendicular to the direction of cyclic stress" (page 585) would suggest that perhaps the attack does assume an intercrystalline character. This fact, were it established, would serve to correlate the author's observations with those made by other workers along somewhat related lines, a correlation which is lacking at present.

H. W. GILLET, Washington, D. C.—I think this can all be summed up in the fact that Rawdon feels that it would clarify this matter if attention were paid to the question of intercrystalline attack, that the sharpness of the notch which forms under corrosion is of such vital importance that when there is intercrystalline attack there is an almost infinitely sharp notch and it would seem as if the problem might be somewhat simplified if we considered it on that basis.

I would inquire whether after all we have not just one endurance limit, the endurance limit of the material. Cannot these notching limits and corrosion-fatigue limits and prior corrosion-fatigue limits which vary with the environment all be summed up in the depth and sharpness of the notch which you get under conditions of corrosion?

I can easily see that with corrosion under stress there would be notching with a very much sharper tool than there would be with corrosion without stress. After all, if we think of it along that line would it not somewhat simplify what appears to be a rather complex proposition? I would also like to register a mild protest against giving any kind of fatigue limit on aluminum alloys on a basis of 100,000,000 cycles. That was borne in on us forcibly very recently when we had a break at 335,000,000 on a duralumin specimen with the endurance limit not reached.

H. F. MOORE, Urbana, Ill.—I would like to report some tests of heat-treated chrome-nickel steel. The specimens were divided into four groups. In group *A* the specimens were left as machined. In group *B* the machined specimens were protected by a coating of rubber cement. In group *C* the specimens were protected by a coating of elastic varnish. In group *D* the specimens were protected by a special varnish. Under the action of a stream of fresh water, the endurance limit of the unprotected specimens was very distinctly lowered from the value for the endurance limit in air. The endurance limit of each of the protected specimens under a stream of fresh water was practically the same as the endurance limit in air.

I acknowledge freely that, in considering the structure of behavior of our metals, we who are engineers must henceforth think about solution potentials and various

other chemical phenomena which, up to the present time, have caused us no concern. Undoubtedly our troubles have been increased by Dr. McAdam's work. I wish to point out, with equal emphasis, that the chemists must now think of problems of stress distribution, which, up to the present time, have caused *them* no concern. As Dr. McAdam and Dr. Gillett have pointed out, the damage done by corrosion is, to a large extent, a question of the particular shape of bite which is taken out of the metal. If corrosion takes rounded bites, such bites as you take out of a biscuit, the damage is relatively small. If the bite is a sharp gash like a knife-cut, the damage is much greater. Both in the study of fatigue of metals without corrosion and in Dr. McAdam's work, the stress concentration factors actually found due to notches—whether mechanical notches or corrosion notches—are not so high as we should expect from the mathematical theory of elasticity. In other words, the theoretical studies of the mechanical effect of notches give results which are on the safe side.

R. L. TEMPLIN, New Kensington, Pa.—The author of this very commendable paper has at his command such a mass of data that it is somewhat hazardous perhaps to take exception to any of his statements. However, I have a few points I would like to bring up for discussion.

If a comparison be made of the fatigue and the corrosion-fatigue limits of commercially pure aluminum, as given in Part V of the present paper and similar values indicated in a previous paper by Dr. McAdam,⁹ some differences will be found. The fatigue limit in the previous paper of $1\frac{1}{8}$ -in. dia., commercially pure aluminum rod was given as 8200 lb. per sq. in., while for a 1-in. dia. rod, having the same static mechanical properties, a fatigue limit of 10,200 lb. per sq. in. is indicated in the present paper.

This difference perhaps may be attributed to the number of cycles used in determining the fatigue limit in the two instances. In the first case the limit was based on results after 250,000,000 cycles. In the second after 55,000,000 cycles.

Our own work on similar and identical material gave an endurance limit of 8000 lb. per sq. in. based on 500,000,000 cycles. The corrosion-fatigue limits for the same material, as indicated by Dr. McAdam, likewise show an appreciable difference, both corrosion-fatigue limits were determined on the basis of 50,000,000 cycles and were 4700 and 5200 lb. per sq. in. for the $1\frac{1}{8}$ and 1-in. dia. rods, respectively. Still different results might well have been obtained had the tests been carried out further.

If the fatigue limit of 8200 lb. per sq. in. is compared with the corrosion-fatigue limit of 4700 lb. per sq. in. as indicated in the paper, damage from corrosion would be much less and the conclusions in the last paragraph on page 597 would not hold. For 25 days' corrosion time the fatigue curve would then be above the corrosion-fatigue curve and not below as indicated. In view of these discrepancies, it would appear necessary to make further tests carried out to a greater number of cycles before the conclusions concerning the pure aluminum and the manganese-aluminum alloy are finally formulated.

T. S. FULLER, Schenectady, N. Y. (written discussion).—Dr. McAdam's paper, in which he has added the concept of prior corrosion-fatigue to the already complicated subject of corrosion fatigue, is extremely important. The tendency of investigators to carry on experiments more nearly under operating conditions is to be commended.

The great difference in the relation of corrosion-fatigue limit to fatigue limit, and the difference in magnitude of the effect of prior corrosion-fatigue between those metals and alloys which tend to form pits, and those which do not, is very striking to those who have given thought to the general topic of corrosion.

⁹ D. J. McAdam, Jr.: Corrosion Fatigue of Non-ferrous Metals. *Proc. A. S. T. M.* (1927).

One factor which may well be considered as a cause contributing to place the corrosion-fatigue limit of ferrous materials below the fatigue limit, and which to my knowledge has not heretofore been mentioned, is the absorption by the steel of an appreciable amount of the hydrogen, resulting from the reaction of the aqueous corroding medium upon the latter. It is well known that a portion of the hydrogen liberated at an iron surface penetrates that surface and diffuses through considerable thicknesses. For instance, a steel tube 12 in. (30.5 cm.) long, and having an outside diameter of $1\frac{1}{16}$ in. (175 mm.) and a wall thickness of $\frac{1}{16}$ in. (16 mm.), and filled with mercury discharged from its inner surface 0.60 c.c. of hydrogen during immersion in Schenectady tap water for 188 hr. at a temperature of 50° C.

It is further known from the work of numerous investigators including Andrew,¹⁰ Stromeyer,¹¹ Parr¹² and Merica,¹³ that the absorption of nascent hydrogen by steel produces brittleness and low fatigue strength.

Would it not be well, therefore, to think over Dr. McAdam's results on the ferrous alloys in the light of nascent hydrogen absorption, and to endeavor to determine, if possible, to what extent, if any, the lowering of the fatigue limit by corrosion is due to this factor?

R. J. MCKAY, New York, N. Y. (written discussion).—Since Dr. McAdam startled us a year or so ago with his experiments showing that the fatigue limit of a metal specimen under corrosive conditions is a figure considerably lower than the endurance limit of the metal in the air, he has studied the phenomenon in much greater detail. In elaborating on it he obtains corrosion-fatigue limits of various values depending on the metal, the corrosive conditions, the speed of revolution, the ratio of pit depth to specimen diameter, and prior corrosion effects. This seems at first glance to so complicate the endurance limit and corrosion-fatigue limit as to make them more difficult of practical use. However, it is my belief that this is only a temporary condition due to the fact that his experiments are not entirely complete and that we will find as the subject is further studied by Dr. McAdam, and I hope others, that the laws governing corrosion-fatigue will become clear and we will be able to predict a service of metals under alternating stress and corrosion with an accuracy never reached in the past.

Probably the present haziness of the results is due to the failure in this present paper to summarize them. All data are given under the head of special metals and the tendency is for a busy reader to read only those parts of the paper covering metals in which he is especially interested. This leaves one with too vague an idea as to the general status of Dr. McAdam's knowledge of this subject. Apparently the knowledge is increased to a considerable extent by these tests and it seems that a general summary would enable one to draw conclusions as to the practical application of results. In view of the above it is possible that some of the questions I ask have been directly answered in the data given in the paper, but in spite of this I will ask them of Dr. McAdam, because he is in a position to interpret the rather complicated data.

The fact that the title of this paper is considerably changed from the titles of former publications may be significant. In this title, "corrosion" of metals is the modified subject instead of "fatigue" as in former papers. Does this mean that the

¹⁰ J. H. Andrew: Embrittling of Iron by Caustic Soda. *Trans. Faraday Soc.* (1914) 9, 316.

¹¹ C. E. Stromeyer: Fatigue of Metals. *Proc. Roy. Soc.* (1914) A90, 411.

¹² S. W. Parr: Embrittling Action of Sodium Hydroxide on Soft Steel. Univ. Illinois Engr. Exp. Sta. *Bull.* 94 (1917).

¹³ P. D. Merica: Embrittling Action of Sodium Hydroxide on Mild Steel, etc. *Met. Chem. Eng.* (1917) 16, 496.

results show a logical effect on corrosion type or corrosion rate by cyclic stress and time; if so, what is the general effect observed and is it the same in all metals; if not, can it be expressed in terms of metal groups? Can Dr. McAdam summarize the effect on rate and type of pitting of (a) corrosion without stress, (b) corrosion below the corrosion-fatigue limit, and (c) corrosion during fatigue. Does a corrosion-fatigue test produce pitting in cases where it would otherwise be entirely absent?

Possibly the above questions would be answered by a more complete explanation of the double curvature in the graphs plotting fatigue limit of the second stage against stress in the first stage (page 583) and stress concentration ratio against stress in the first stage (page 586).

What general conclusions are to be drawn from the rate of revolution? Is the corrosion-fatigue limit in the same corrosion conditions raised or lowered with increase or decrease in number of revolutions? Is the effect the same in all metals or can it be classified according to the metal types?

It is possible with a given metal and a given solution to control corrosion rates; for instance, with monel metal and sulfuric acid under practical conditions the concentrations can be adjusted so that the corrosion rate will vary from 20 mg. per sq. dm. per day to 200 mg. per sq. dm. per day and by varying the oxygen concentration and velocity of movement in laboratory tests from 1 mg. per sq. dm. per day to 500 mg. per sq. dm. per day. Any given rate can be duplicated within possibly 10 per cent. What would be the result if corrosion-fatigue tests were made under such varying corrosion rates? Also, in certain solutions, it is possible to corrode a metal evenly or to produce pitting during the corrosion. What would be the result of running corrosion-fatigue tests under these variations?

The lowering of the fatigue limit by corrosion is different for different metals. Is it possible at present to connect the degree of lowering with the rate of corrosion, the type of corrosion or any physical properties, or ratio of the physical properties of the metals? In other words, what general conclusions are to be drawn as to the types of metals most resistant to corrosion-fatigue?

T. M. JASPER, Milwaukee, Wis. (written discussion).—Dr. McAdam has shown that stressless corrosion prior to fatigue has not as much effect as has simultaneous corrosion with fatigue. The writer has found that corrosion under static stress has greater effect than corrosion without stress. This effect becomes more pronounced as an approach to the static yield point is reached. When the yield point is reached, corrosive effect is increased very much.

It would be appropriate in connection with corrosion-fatigue if the relation between the diameter of a specimen or shaft and the value of the fatigue limit under corrosion was carefully established. Until this is done the value of corrosion-fatigue for large shafts such as are used on ships cannot be correctly arrived at and applied. For a particular steel it is not supposed that the same proportional decrease of fatigue limit due to corrosion exists in a large specimen as in a small specimen. Should such seem to be the case it would suggest that a corrosion-fatigue limit does not really exist.

It is believed that if a corrosion-fatigue limit exists, mathematically the values can be somewhat anticipated for various sizes of specimens. However, it is also believed that this should be established experimentally before it can be used with reliability.

W. B. PRICE, Waterbury, Conn. (written discussion).—We have recently encountered what was at the time a baffling case of premature fatigue failure. Certain articles of low brass, which usually withstood 100,000 bending reciprocations without failure, cracked in specific cases, upon less than 10,000 reciprocations. An investigation revealed that while the general surface of the article did not seem to be appreciably corroded, the fatigue cracks were decidedly discolored and in our estimation quite definitely corroded.

Dr. McAdam's paper has convinced us that these failures were due to corrosion-fatigue and precautions have accordingly been taken which we hope will prevent recurrence of the trouble. We extend our thanks to Dr. McAdam for presenting his work before the Institute of Metals Division, for we believe that this aspect of fatigue will prove to be of very great importance.

D. J. McADAM, JR. (written discussion).—Dr. Rawdon's statement that "the severity of the corrosive attack, at least as ordinarily measured, is directly proportional to the length of the corrosion period" is, I believe, not generally correct. The effect of time on the rate of corrosion depends largely on the character of the surface film. Some films are protective, others tend to accelerate corrosion. As pointed out in the paper, a carbonate water has a decidedly protective action against stressless corrosion of steel.

It may be true in special cases that the loss in weight is proportional to corrosion time. Even in such cases, however, it should not be assumed that the fatigue limit would fall at a uniform rate or that the stress-concentration ratio would rise at a uniform rate.

His incorrect assumption in regard to the effect of prior-corrosion time on the fatigue limit leads Dr. Rawdon to an unwarranted implication in regard to the surface finish of the specimens used in the investigation; in spite of the statement on page 574 of the paper that the surface finish was "sufficiently smooth to permit examination of the structure at a magnification of 100." As this statement with the accompanying references distinctly implies, there were in these specimens no more effects of machining, grinding, etc., than in any well prepared metallographic specimens. Etching of these fatigue-test specimens reveals no such defects as Dr. Rawdon imagines.

Investigation at the Naval Experiment Station several years ago showed that removal of the surface film by etching does not appreciably lower the fatigue limit. After reading Dr. Rawdon's discussion, however, a previously polished specimen was selected at random, etched with nitric and picric acids, and examined under the microscope at a magnification of 100. The microstructure revealed by this etching was free from distortion and the surface was free from scratches. Subsequent test of this specimen showed that its fatigue limit had not been lowered by the etching. The graphs in Fig. 11, therefore, are undoubtedly a true representation of the effect of time on stressless corrosion.

It is worthy of note that the experiments of R. R. Moore on thin-walled tubes of duralumin show the same decreasing effect of time on stressless corrosion. The fatigue limit was lowered nearly as much by five days' corrosion in salt spray as by ten days' corrosion.

Metallographic studies of corroded specimens will be made as opportunity permits. In the meantime there would seem to be no valid objection to discussion of duplex alloys such as Muntz metal and chromium-vanadium steel in the same paper with alpha solid solutions.

Dr. Rawdon and Dr. Gillett have, I believe, overemphasized the importance of deciding at this time whether or not the origin of notches or cracks (under simultaneous corrosion and cyclic stress) is in the intercrystalline boundaries. As stated by the author in reply to discussion of previous papers, the corrosion-fatigue cracks do not follow intercrystalline boundaries. As stated in the present paper, the notches formed below the corrosion-fatigue limit are perpendicular to the direction of tensile stress. The notches in steel at least do not follow intercrystalline boundaries.

The notches and cracks undoubtedly start at regions where stress and corrosion intensity are greatest. Such regions, sometimes at least, are non-metallic inclusions. Possibly in some cases the notches start at grain boundaries or at slip lines within the grains. Of primary importance, however, is the influence of cyclic stress on the depth

and sharpness of the notches and on the fatigue limit. Whether the notches start at intercrystalline boundaries or elsewhere is of secondary importance.

Dr. Gillett's discussion of the effect of notches on the relation between endurance limit, corrosion-fatigue limit and notching limit does not "simplify" these subjects. In reply to his surprising question whether there is not "just one endurance limit, the endurance limit of the material" I would say that the analysis of the corrosion-fatigue process on the second page of the paper is based on the assumption that there is only one endurance limit. The discussion on "stress concentration" and related subjects on pages 583 to 587, and in other parts of the paper, is based on the same assumption. Are not the ordinates of the graphs in Figs. 3, 11 and 12 based on the same assumption?

In the remainder of Dr. Gillett's discussion of the effect of depth and sharpness of notches, he merely paraphrases the discussion of this subject in the paper. It should be pointed out, however, that the "notching limit" does not depend on the endurance limit.

I do not agree with Dr. Gillett that it is necessary to continue endurance tests of duralumin beyond 100 million cycles in order to determine the endurance limit. Owing to "scatter," the stress-cycle graph for duralumin is usually a relatively broad band curving downward toward a horizontal asymptote. Beyond 100 million cycles this band is so nearly horizontal that the endurance limit can be determined for all practical purposes by determining the position of the band at 100 million cycles or even at 50 million cycles. Within the range of stress represented by the nearly horizontal part of this band, some specimens will break at 50 million cycles. Others would break at 50 billion cycles if experiments could be continued so long.

Mr. Fuller speaks of nascent hydrogen absorption in relation to ferrous alloys. In discussion of a previous paper, Dr. Speller suggested the possibility that nascent hydrogen may be responsible for the damages to steel under corrosion-fatigue. At that time, corrosion-fatigue of non-ferrous metals had not been investigated by the author. The fact that corrosion-fatigue damages non-ferrous metals seems to indicate that embrittlement by nascent hydrogen is not an essential factor in corrosion-fatigue. The fact that between the two stages of a prior-corrosion fatigue test there is sometimes a time interval of several days, indicates that nascent hydrogen is not a factor in the second stage. It has been shown in the paper that the damaging effect of corrosion-fatigue is due to the formation of sharp notches, which are due to an unexplained effect of cyclic stress on corrosion.

Much of the damage that has heretofore been ascribed to hydrogen "embrittlement" is undoubtedly due to corrosion-fatigue. It is doubtless possible to obtain hydrogen embrittlement in the laboratory, but the possibility of hydrogen embrittlement under service conditions has, I believe, been overestimated.

As suggested by Mr. McKay, a summary to the paper would have been desirable. On account of the size of the paper, a summary was not included, but was published later in *MINING AND METALLURGY* (March, 1928).

Mr. McKay is correct in his idea that the paper shows the effect of cyclic stress and time on corrosion. The ordinates of the graphs in Figs. 3, 11 and 12 are an index of the depth and sharpness of pitting and the forms of the graphs illustrate the effect of cyclic stress-range, time and number of cycles on corrosion pitting. As shown in Fig. 3, the effect varies with the electrochemical properties of the metal. For "low-potential" alloys, pitting is negligible below a fairly definite limit, which may be called either "pitting limit" or "notching limit."

The outward curvature after the first steep descent of the graphs for chrome-vanadium steel is due in part to decrease in corrosion intensity at the bottoms of corrosion pits, in part to local elevation of the endurance limit at the bottoms of the pits, and in part to another factor which will be discussed in a later paper.

The effect of cycle frequency on the corrosion-fatigue limit has not been thoroughly investigated. Increase in time per cycle, however, probably lowers this limit.

Part VII presents results of a preliminary investigation of the effect of cycle frequency on corrosion. These results indicate that the penetration per cycle increases with increase in cyclic stress-range, and with increase in time per cycle. The time rate of penetration, however, increases with increase in cyclic stress-range, and with increase in cycle frequency. These conclusions apply only to pitting before depth limitation becomes prominent. Investigation of pitting rates is being continued and in time it may be possible to answer Mr. McKay's other questions on this subject.

In reply to his last question I would say that metals that are most resistant to stressless corrosion are usually most resistant to corrosion-fatigue.

I do not understand the logic of Professor Jasper's argument that if the corrosion-fatigue limit is a variable, it "does not really exist." That the corrosion-fatigue limit varies with corrosion conditions has been shown in previous papers; that it varies with cycle frequency seems probable. In the present paper it is suggested that the corrosion-fatigue limit is affected by diameter or thickness of specimen. That a corrosion-fatigue limit exists, however, numerous stress-cycle graphs bear evidence.

Mr. Templin compares the results of endurance tests on commercial aluminum as presented in this paper with results obtained with another sample of aluminum and presented in a previous paper. He concludes that the higher results in the present paper are due to the fact that recent tests were not continued beyond 100 million cycles. A study of the graph for material IMB in Fig. 8, however, will show that the horizontal asymptote could not possibly be 2000 lb. per sq. in. lower, no matter how far the curve is extended. A curve that descends only about 300 lb. per sq. in. between 10 million and 100 million cycles has for all practical purposes reached its endurance limit at 100 million cycles. Similar comment applies to the curve in a previous paper to which Mr. Templin refers. The different results obtained with the two samples of aluminum, therefore, are evidently due to a real difference in the material.

Even if Mr. Templin's explanation were correct, however, the conclusions expressed in the last paragraph on page 597 would not be altered.

The corrosion-fatigue graph for aluminum may slope downward even beyond 50 million cycles. This, however, does not alter the conclusions expressed in the paper. These conclusions were based on the fact that 25 days' corrosion without stress gave as low results as 25 days' corrosion with stress at the corrosion-fatigue limit. The same relation would probably hold if comparison were made after longer corrosion time.

Aluminum-beryllium Alloys

By R. S. ARCHER* AND W. L. FINK,* CLEVELAND, OHIO

(New York Meeting, February, 1928)

THIS paper describes results obtained on aluminum-beryllium alloys and aluminum-beryllium-copper alloys in the preparation of which aluminum of 99.95 per cent. purity was used. The constitution and structure of the high purity binary alloys are given. The aluminum-beryllium eutectic occurs at 0.87 per cent. beryllium and 645° C. The solid solubility of beryllium in aluminum at 631° C. is 0.05 per cent. beryllium, and at room temperature is less than 0.013 per cent. beryllium. The densities of the alloys are substantially the same as the values calculated on the assumption that the densities of the elements are not changed by alloying. All of the alloys age-harden at room temperature after a solution heat treatment, and the chill cast aluminum-beryllium-copper alloys age-harden at room temperature without a prior solution heat treatment. Hardness and tensile properties are given. Salt spray corrosion tests on sheet specimens are described. It is shown that beryllium does not lower the corrosion resistance of aluminum to salt spray provided the alloy has received a solution heat treatment.

COMMERCIAL POSSIBILITIES OF BERYLLIUM ALLOYS

Beryllium has certain properties such as low density, high hardness, good corrosion resistance, low thermal expansion and fairly good electrical conductivity, which would indicate that it is worthy of consideration as an ingredient of light alloys. It was not until recently, however, that beryllium could be produced with sufficient ease to encourage research along this line. The production of beryllium by electrolysis from a fluoride bath has now developed to the stage where it could be used commercially if there were sufficient demand for the element.

Claims made in certain newspapers and technical articles in regard to the strength and corrosion resistance of the aluminum-beryllium alloys are not justified by experimental results. Moreover, beryllium is an expensive metal (\$200 a pound at the time this work was done) and, on account of the nature of its ore and the consequent difficulty of its extraction, it will in all probability continue to be a relatively expensive metal, although the cost would undoubtedly be a great deal less than \$200 a

* Metallurgical Division, Research Bureau, Aluminum Co. of America.

pound if the metal were produced on a large scale. It seemed, therefore, that low-beryllium alloys offered the greater commercial possibilities except for very special purposes. It was partly for this reason that in the present work emphasis has been placed on beryllium alloys of low beryllium content.

PROPERTIES OF BERYLLIUM

Beryllium is a divalent element which has the atomic number 4 and occurs in the second group of the periodic system. G. P. Thomson¹ and Aston² have examined beryllium for isotopes by the positive-ray analysis and found it to be a simple element with an atomic weight of 9. Beryllium is one of the lightest metals, having a density of 1.84 according to the work of Fichter and Jablczynski.³ The melting point is high (1278° C. according to Oesterheld⁴). The boiling point has not been determined, but Vivian⁵ reports that it is evidently not far above the melting point.

According to McKeehan⁶ the beryllium space lattice is hexagonal close packed, having the dimensions $a = 2.283\text{\AA}$ and $c = 3.607\text{\AA}$, which corresponds to the axial ratio 1.580.

The hardness of beryllium has been determined by several workers. According to Fichter and Jablczynski³ the scratch hardness is 6 to 7 on Moh's scale. The Rockwell hardness of the beryllium used in the present investigation was 81 on the "B" scale. Vivian⁵ found an average Brinell hardness of 140 for beryllium obtained by electrolysis and for the first and second sublimates obtained from it. Later sublimates showed a lower hardness—even as low as 90.

All specimens of the metal that have been described are brittle at room temperature, and to the authors' knowledge, there is but one case on record of a sample of beryllium being worked at any temperature. Fichter and Jablczynski⁷ have reported this as follows: "No ductility could be observed at ordinary temperature; the metal is brittle and falls apart when hammered. At higher temperatures it becomes ductile. A beryllium 'regulus' was laid between two pieces of cast steel, all three pieces raised to a red heat, and then pressed together in a vise. There was formed a flat piece of beryllium which left its imprint in the surface of the steel."

During the course of the work described in this paper, it was found that light blows on a piece of beryllium while it was in a furnace at 1070° C. would sometimes cause local deformation without cracks but the piece

¹ *Phil. Mag.* (1921) **42**, 857.

² *Nature* (1923) **111**, 739.

³ F. Fichter and K. Jablczynski: Über Beryllium Metall. *Ber. der deutsch Chem. Gesell.* (1913) **46**, Pt. 2, 1604.

⁴ *Zeitschr. anorg. Chem.* (1916) **97**, 1.

⁵ A. C. Vivian: Beryllium. *Trans. Faraday Soc.* (1926) **22**, 211.

⁶ *Proc. Nat. Acad. Sci.* (1922) **8**, 270.

⁷ *Op. cit.*, 1609.

was so brittle that no rolling or forging operations could have been carried out. Both higher and lower temperatures were tried with even less encouraging results. It may be, however, that extremely pure beryllium is sufficiently plastic to be worked at a suitable temperature, probably about 1070° C. It is interesting in this connection that when an aluminum-beryllium alloy containing 23 per cent. by weight of beryllium is cold rolled, the primary beryllium constituent is deformed very considerably without any cracking (see section on Structure of Aluminum-beryllium Alloys). According to Oosterheld this constituent is not pure beryllium but contains about 8 per cent. of aluminum in solid solution.

TABLE 1.—Average Coefficients of Expansion of Beryllium Per Degree Centigrade*

Temperature Range, Deg. C.	Coefficient of Expansion, $\times 10^{-6}$	Temperature Range, Deg. C.	Coefficient of Expansion, $\times 10^{-6}$
-100 to - 50	7.0	+20 to +300	14.0
-120 to + 20	8.1	+20 to +400	14.8
- 50 to + 20	9.8	+20 to +500	15.5
+ 20 to +100	12.3	+20 to +600	16.1
+ 20 to +200	13.3	+20 to +700	16.8

* Bur. of Stds. *Tech. News Bull.* No. 118 (Feb., 1927.)

TABLE 2.—Physical Constants of Beryllium

Constant	Value	Authority
Atomic number.....	4	
Valence.....	2	Nilson and Pettersson
Atomic weight.....	9.018 ± 0.002	Hönigschmid
Atomic weight.....	9.000 ± 0.009	Aston
Atomic radius.....	1.00 Å°	Huggins
Lattice.....	Hexagonal close-packed	McKeehan
Axial ratio.....	1.58	McKeehan
Specific gravity at 20° C. compared to water at 20° C.....	1.842	Fichter and Jablczynski
Atomic volume.....	4.90	
Melting point.....	1278° C.	Oosterheld
Scratch hardness.....	6 to 7 (Moh's Scale)	Fichter and Jablczynski
Rockwell hardness.....	81 (B scale)	Obtained in this investigation
Brinell hardness.....	140 (Electrolytic Be)	Vivian
Brinell hardness.....	90 (Sublimed Be)	Vivian
Electrical conductivity.....	5.41×10^4 (20° C.) Reciprocal ohms	Fichter and Jablczynski
Specific heat.....	0.4246 at 100.07° C.	Nilson and Pettersson
Heat of fusion.....	277 Cal	Oosterheld
Heat of oxidation.....	151.5 Cal	Copaux and Philips
Coefficient of expansion.....	See Table 1	Bureau of Standards

The coefficient of thermal expansion of beryllium is very nearly the same as that of iron. The Bureau of Standards, using beryllium from the same source as that used in this work, obtained the values given in Table 1, which is taken from the *Technical News Bulletin* of the Bureau of Standards. A number of the physical constants of beryllium are given in Table 2.

LITERATURE ON ALUMINUM-BERYLLIUM ALLOYS

Several articles and patents on aluminum-beryllium alloys are listed in Table 3. Of these, the articles by G. Oosterheld, W. Kroll, and P.

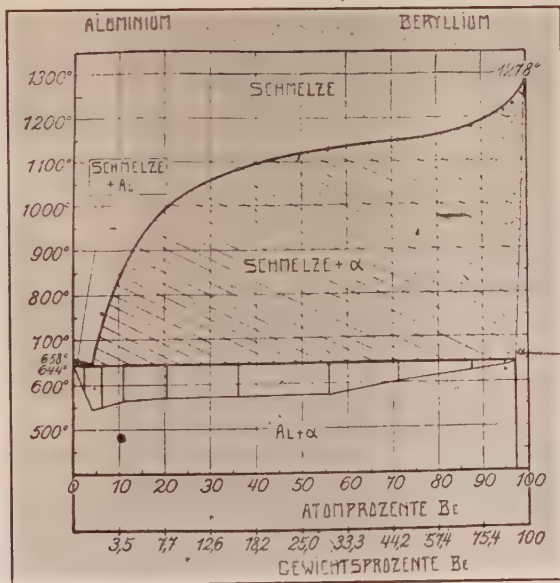


FIG. 1.—AL-BE CONSTITUTION DIAGRAM ACCORDING TO OOSTERHELD.

Hidnert and W. T. Sweeney are believed to give the most reliable and most extensive data.

Oosterheld investigated the constitution and structure of the binary aluminum-beryllium alloys. Thermal and microscopic analyses were made on approximately 0.5-gm. samples, which were prepared in a hydrogen atmosphere from electrolytically reduced beryllium and 99.8 per cent. aluminum. Two cooling curves and one heating curve were taken for each sample and the corrected temperatures obtained from the second cooling curve were used together with the results of microscopic investigation to construct the equilibrium diagram shown in Fig. 1. The eutectic temperature was found to be 644° C. and the eutectic composition to be 1.4 per cent. beryllium and 98.6 per cent. aluminum by weight. The solid solubility of aluminum in beryllium was found to

be slightly less than 8 per cent., and that of beryllium in aluminum less than 0.4 per cent. by weight.

TABLE 3.—*Articles and Patents on Aluminum-beryllium Alloys*

Author	Title	Reference
C. H. Ivinson.....	Alloying Aluminum with the Rarer Metals	<i>Foundry</i> (1913) 41 , 321. <i>Metal Ind.</i> (1913) 11 , 340.
Oosterheld.....	Alloys of Beryllium with Aluminum, Copper, Silver and Iron	<i>Zeitschr. anorg. Chem.</i> (1916) 97 , 6.
H. S. Cooper.....	Alloys of Aluminum with Beryllium	Am. Pat. 1254987
Cooper Co.....	Alloys	Brit. Pat. 120565
Fahrenwald.....	Alloys of Al and Be and Similar Alloys	Am. Pat. 1333965
Fahrenwald.....		Ger. Pat. 386301
Metallbank.....		Brit. Pat. 155805
G. J. Kroll.....		U. S. Pat. 1359813
G. J. Kroll.....		Brit. Pat. 164608
T. Goldschmidt Akt.-Ges.....		Brit. Pat. 221083
Metallbank.....		Brit. Pat. 192414
E. A. Engle and B. S. Hopkins....	Electrolytic Production of Beryllium, and Metallurgy and Alloys of Beryllium	<i>Trans. Am. Electrochem. Soc.</i> (1924) 45 , 475.
Anonymous.....	Beryllium and Its Possibilities as an Alloying Metal	<i>Iron Age</i> (1926) 117 , 220.
W. Kroll.....	The Mechanical Properties of the Binary Aluminum-Beryllium Alloys	<i>Metal und Erz.</i> (N. F. XIV) (1926) 23 , 616.
W. Kroll.....	Improvable Aluminum Alloys	<i>Metal und Erz</i> (N. F. XIV) (1926) 23 , 613.
P. Hidnert and W. T. Sweeney....	Thermal Expansion of Beryllium and Aluminum-Beryllium Alloys.	Bureau of Standards <i>Sci. Paper</i> 565

Oosterheld noted that the eutectic consists of much aluminum and a little beryllium which is in the form of fine needles. In hypereutectic alloys no eutectic structure was observed, and this was explained by Oosterheld as being due to the eutectic beryllium crystallizing on the primary beryllium constituent. He also noted that the form of the primary beryllium constituent varies with the beryllium content of the hypereutectic alloys. This will be referred to again.

Dr. W. Kroll has published two articles on aluminum-beryllium alloys (see Table 3). The samples used in the study of mechanical properties were sheet tensile specimens about 1 mm. thick, which had been heated at 420° C. (788° F.). Table 4 gives the composition of the

TABLE 4.—*Mechanical Properties of Binary Aluminum-beryllium Alloys*
According to Kroll

Composition, Per Cent.			Strength, Pounds per Square Inch	Elongation, Per Cent.	Brinell Hardness as Cast 500 Kg. 10- Mm. Ball	Remarks
Si	Fe	Be				
Maximum 0.1	0.40	0.30	11,100	34.5	25.5	Pure aluminum
	0.45	1.30	12,660	34.5	29.0	
	0.55	2.06	13,230	30.5	30.5	
	0.84	6.06	16,410	31.8	33.0	
	2.70	9.87	18,080	21.5	36.0	
	1.35	20.23	22,900	8.9	39.0	
	0.65	8.65			34.5	
	0.25		9,250	37.5	22.5	

TABLE 5.—*Average Coefficients of Expansion of Beryllium and Aluminum-beryllium Alloys*
Hidnert and Sweeney

Material	Average Coefficients of Expansion per Degree Centigrade				
	20° to 100° C., X10 ⁻⁶	20° to 200° C., X10 ⁻⁶	20° to 300° C., X10 ⁻⁶	20° to 400° C., X10 ⁻⁶	20° to 500° C., X10 ⁻⁶
Beryllium (98.9 per cent.).....	12.3	13.3	14.0	14.8	15.5
Aluminum-beryllium alloy (4.2 per cent. Be).....	22.2	23.2	24.4	25.1	26.5
Aluminum-beryllium alloy (10.1 per cent. Be).....	21.4	22.5	23.3	24.1	25.4
Aluminum-beryllium alloy (18.6 per cent. Be).....	20.0	20.8	22.1	23.0	24.0
Aluminum-beryllium alloy (27.5 per cent. Be).....	18.8	19.8	21.1	22.0	23.0
Aluminum-beryllium alloy (32.7 per cent. Be).....	17.9	19.2	20.6	21.3	22.3

specimens, the results of tensile tests, and the Brinell hardness of the chill cast ingots (40 mm. sq.) from which the sheet was rolled. In regard to these results, Kroll states, "The effect of beryllium on the mechanical properties of aluminum is comparable to that of silicon in aluminum, but a given per cent. of beryllium has less effect than an equal amount of

silicon. The binary aluminum-beryllium alloys do not possess technical importance as far as this investigation extends."

In the second article, Kroll states that binary aluminum-beryllium alloys age-harden after suitable heat treatment, and the aging was explained on the basis of a solubility of beryllium in aluminum that is a function of the temperature. Kroll states, "The solid solution of beryllium in aluminum therefore amounts to as much as 0.3 per cent. at 640° C. . . . Probably the solubility limit at room temperature lies under 0.2 per cent." In regard to the more complex alloys, magnesium was shown to change the solubility of beryllium in aluminum without destroying the age-hardening effect. It was found that magnesium and beryllium do not form a compound in the Al-Be-Mg alloys. Silicon decreased the age-hardening effect, although no compound between beryllium and silicon was found. Aluminum-beryllium alloys containing 4.5 per cent. copper with or without magnesium age-hardened appreciably at room temperature after a solution heat treatment. On summarizing the effects of the addition of beryllium to commercial alloys, Kroll states. " . . . an addition of a maximum of 1 per cent. beryllium to the Lautal and Aludur metals can be indicated as useful. Beryllium is to be considered as a substitute for silicon in the results attained, but not in the compound Mg_2Si . Whether the small improvement of the mechanical properties obtained by small additions of beryllium, which is still very expensive, is of practical value considering the price, can be decided only by technology."

The paper by P. Hidnert and W. T. Sweeney (see Table 3) gives results on the linear thermal expansion of beryllium (98.9 per cent.) and five aluminum-beryllium alloys containing various percentages of beryllium (4 to 33 per cent.). The results on beryllium have been given above and a summary of those on aluminum-beryllium alloys is given in Table 5. The coefficients of expansion on the first heating were smaller than those on subsequent heatings, on account of a permanent shrinkage of 0.01 to 0.03 per cent.

MATERIALS USED IN PRESENT INVESTIGATION

The beryllium was purchased from the Beryllium Corp'n. of America and, according to H. S. Cooper of that company, it contained 0.89 per cent. iron, 0.10 per cent. silicon, no aluminum, and no magnesium. The metal was produced electrolytically from a fluoride bath, and remelted under a barium chloride flux.

The aluminum used for most of this work was made by the electrolytic refining method of Hoopes,⁸ and by analysis contained 0.01 per cent.

⁸ Francis C. Frary: The Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) **47**, 275.

copper, 0.02 per cent. iron, and 0.02 per cent. silicon. This material will be referred to as 99.95 per cent. aluminum. For a few of the samples commercial Hall-process aluminum was used, containing by analysis 0.16 per cent. copper, 0.51 per cent. iron, and 0.18 per cent. silicon. This material will be referred to as 99 per cent. aluminum.

The copper was cathode copper, the iron was Armco iron wire, the magnesium was sublimed magnesium of 99.98 per cent. purity made by the American Magnesium Corpn.

PREPARATION OF THE ALLOYS

Binary aluminum-beryllium alloys containing from 1 to 23 per cent. of beryllium were most conveniently made in the following manner. The aluminum was melted in a Dixon plumbago crucible and brought to a temperature of 1000° to 1200° C., depending on the per cent. of beryllium being added. A small amount of barium chloride was sprinkled on the surface of the melt and the beryllium dropped in. If the aluminum did not wet the beryllium, a little more barium chloride was added. After wetting had been secured, solution was rapid. The metal was thoroughly stirred and cast into notch bars.

Beryllium-rich alloys made in this way were used in making the alloys containing less than 1 per cent. of beryllium.

Since Oesterheld had reported that beryllium carbide was formed in some beryllium-rich alloys which were melted in carbon crucibles, plumbago crucibles were avoided during the first part of the work. The first small heats were made in aluminum boats in an electric furnace with a hydrogen atmosphere, no flux being used. Later, in making larger heats in a carbon resistor or oil-fired furnace without a hydrogen atmosphere, plumbago crucibles lined with magnesia were used. As the work progressed, aluminum-beryllium alloys containing up to 23 per cent. beryllium were made in plumbago crucibles without a magnesia lining. No beryllium carbide could be observed and the properties of the alloys so produced were comparable with those of alloys produced in magnesia-lined crucibles.

The work was almost completed before the chemical analyses were obtained. A comparison of the composition by mixture and the composition by analysis showed that the beryllium content by analysis was always the lower. Moreover, the use of flux of NaCl and KCl seemed to cause a lowering of the primary beryllium point in a cooling curve. Both BaCl_2 and $\text{NaCl} + \text{KCl}$ fluxes caused the disappearance of beryllium from molten aluminum-beryllium alloys.

As an example of this action, a part of sample 4523, which by analysis contained 1.67 per cent. beryllium, was held at 750° to 850° C. under a flux of $\text{NaCl} + \text{KCl}$ for 3 hr. No beryllium could be found by either

microscopic examination, or chemical or thermal analysis of the resulting material (sample 4529).

Beryllium has a great affinity for chlorine, and the chloride, BeCl_2 , has been prepared by heating beryllium in a stream of dry chlorine or dry hydrogen chloride, or by heating beryllium carbide in either atmosphere. Even beryllium oxide can be converted into the chloride by the action of carbon and dry hydrogen chloride, or of carbon tetrachloride. It seems plausible, then, that sodium, potassium, or barium chloride would react with beryllium to form the chloride BeCl_2 which has a boiling point of 520°C .

It is evident that no more of the flux should be used than is necessary, and that the alloy should not be held molten any longer than is necessary.

Dr. Kroll prepared his alloys at temperatures above the melting point of beryllium and states that a loss of 10 to 20 per cent. of the beryllium must be counted on, because of selective oxidation. He does not mention the use of any flux.

ANALYSIS OF THE ALLOYS

Most of the samples that contained more than 0.2 per cent. beryllium were analyzed by J. A. Boyer in the laboratory of the American Magnesium Corp'n. The compositions of the samples that were not analyzed were calculated from the compositions of the beryllium-rich alloys, as determined by analysis.

The method of analysis used was developed from the method of Britton,⁹ which depends on the fact that NaBeO_2 is completely hydrolyzed in an alkaline solution under conditions that will not cause a precipitation of aluminum. A description of the procedure was furnished by H. E. Bakken of the American Magnesium Corp'n., as follows:

"Weigh 1 gm. of well mixed drillings into a casserole, cover with water and dissolve in 14 c.c. of aqua regia. Add 10 c.c. of 1:1 H_2SO_4 , fume, and separate silicon in the usual manner. Dissolve the residue from the silicon determination in a few drops of concentrated H_2SO_4 and combine with the main solution. If copper is present, it is removed by electrolysis at this point. Neutralize the solution with freshly prepared 6N NaOH and add 13.5 c.c. in excess, stirring until the hydroxides are completely dissolved. Dilute to 500 c.c. and boil for 40 min., adding water to maintain the same volume. Filter immediately through a moderately close filter and wash 20 times with hot water. Ignite in platinum at a bright red heat and weigh as BeO plus Fe_2O_3 . The Fe_2O_3 is determined by fusing the mixed oxides with KHSO_4 and titrating with KMnO_4 .

"In every case, a standard approximating the intended content of the alloys was analyzed with it, and a correction applied. The standards

⁹ H. T. S. Britton: Separation of Aluminum from Beryllium (Serial). *Analyst* (1921) 46, 359, 437.

were made up from pure aluminum and Eimer & Amend C.P. BeCO_3 . The latter contained a mere trace of aluminum by the Haven's test (HCl gas in concentrated ether- HCl solution). The BeCO_3 was evaluated by precipitation from its solution in HCl with NH_4OH and ignition to BeO , and checked by direct ignition of the carbonate. Concordant results were obtained by the two methods.

"Blank tests on the reagents yielded no beryllium.

"The results were computed using 9.02 as the atomic weight of beryllium, or in other words, the factor Be/BeO was taken as 0.3605."

HARDNESS AND AGE-HARDENING OF ALUMINUM-BERYLLIUM ALLOYS

Immediately after casting, Brinell hardness tests were made on slabs $\frac{1}{4}$ -in. thick, of alloys containing from 0.013 to 0.75 per cent. beryllium, cast in an iron mold. Tests were also made after a solution treatment of 24 hr. at 631°C . followed by quenching in water at room temperature, and after various periods of aging at room temperature.

Table 6 gives the Brinell hardness values obtained with 500-kg. load, 10-mm. dia. ball, and 30 sec. application of load.

TABLE 6. *Brinell Hardness of Chill-cast Aluminum-beryllium Alloys*

Per Cent. Beryllium.....	0.75	0.40	0.21	0.075	0.025	0.013
Sample No.....	4319	4334	4333	4332	4354	4355
Immediately after casting.....	25.9	22.8	21.2	19.4	17.2	16.8
Immediately after quenching (631°C).....	27.3	24.1	23.8	22.7	17.2	15.7
Quenched (631°C) and aged 2 days at room temperature.....	42.9	39.1	37.0	36.8	24.3	16.9
Quenched (631°C) and aged 3 days at room temperature.....	42.5	38.8	36.6	36.3	23.4	16.8
Quenched (631°C) and aged 10 days at room temperature.....	42.7	39.0	37.8	36.8	24.6	17.4
Increase due to aging*.....	15.4	14.9	13.3	13.9	6.9	1.3
Per cent. increase due to aging....	56	61	56	61	40	8

* Difference between average of values in rows 3, 4, and 5 and value in row 2.

SOLID SOLUBILITY OF BERYLLIUM IN ALUMINUM

Assuming the validity of the precipitation theory of age-hardening, these results give a close approximation to the solubility of beryllium in aluminum at 631°C . This is shown graphically in Fig. 2. The break in the curve at about 0.05 per cent. beryllium would indicate that only 0.05 per cent. beryllium will dissolve in aluminum under the conditions described. The fact that a slight age-hardening effect is obtained with 0.013 per cent. beryllium indicates that the solubility of beryllium in aluminum at room temperature is less than this amount.

Although it would be very difficult, if not impossible, to determine accurately the solid solubility by microscopic methods on account of the very low solubility and the difficulty of getting a satisfactory polish on such soft specimens, nevertheless a rough check was possible. Beryllium particles could be seen in the microsection of sample 4333 (0.21

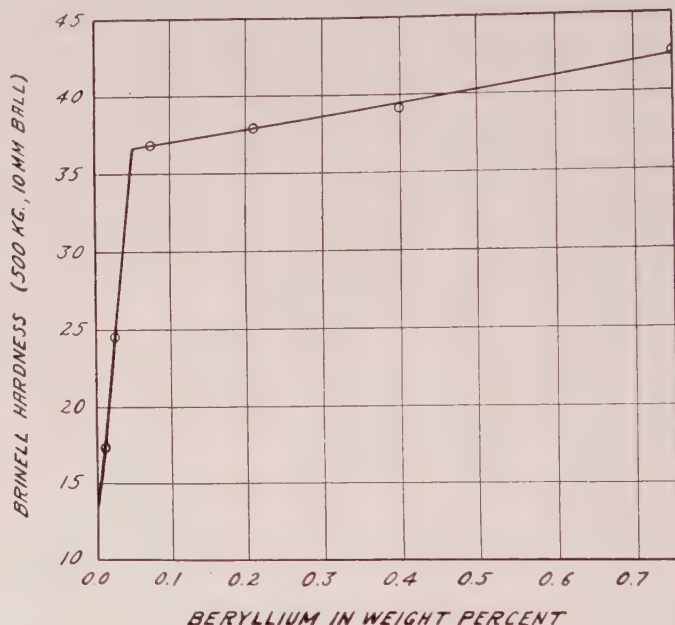


FIG. 2.—BRINELL HARDNESS OF CHILL-CAST SPECIMENS QUENCHED FROM 631° C. AND AGED AT ROOM TEMPERATURE FOR 10 DAYS.

per cent. Be), which had been held at 639° C. for 50 hr. and quenched, but it was very difficult to decide whether all of the small particles in sample 4332 (0.075 per cent. Be) were polishing defects or whether some of them were beryllium. As a result of microscopic examination, it seemed that the solubility of beryllium in aluminum at 639° C. was much nearer 0.075 per cent. beryllium than 0.21 per cent. beryllium.

THERMAL ANALYSIS

Cooling curves were run on five samples of which the beryllium content lay in the range 0 to 2.0 per cent. The samples weighed between 200 and 400 gm. and the procedure used was as follows: The metal was heated in a small Hevi-Duty crucible-type electric furnace to a temperature well above the liquidus (from 750° C. to 900° C. depending on the beryllium content), thoroughly stirred with a tungsten or carbon stirring rod, and

a small amount of it poured into an iron mold which gave samples $\frac{1}{4}$ in. thick for chemical analysis. The rest of the metal was replaced in the furnace and a fused silica protection tube (8 mm. outside diameter, 6 mm. inside), which had been coated with "Blackene" stove polish to protect it from the melt, was inserted so that the end was approximately twice as far from the top of the melt as from the bottom. A layer of finely divided alumina was placed on the surface of the melt, the openings in the furnace top were covered with asbestos sheet, and the metal allowed to soak for a few minutes to insure thermal equilibrium. During this interval, the temperature of the bead of the thermocouple (No. 18 B. & S. gage chromel-alumel couple) was determined simultaneously by means of a calibrated mercury thermometer and by reading the voltage of the couple in order to determine whether or not the cold junction had reached the temperature (0° C.) of the ice and water bath in which it was immersed. The thermocouple was inserted in the protection tube, the furnace current shut off, and the cooling curve followed with a Leeds and Northrup type K potentiometer, as the metal cooled in the furnace at approximately 2° C. per minute. The thermocouple was frequently checked at the freezing point of the 99.95 per cent. aluminum (660° C.).

The primary beryllium points were weak, especially for the 1.34 per cent. beryllium sample, and may be low on account of undercooling. An attempt was made to determine the extent of undercooling by taking a heating curve, but the primary beryllium point could not be detected at all on the heating curve. The eutectic arrest occurred at the same temperature on the heating and cooling curves.

REVISED CONSTITUTION DIAGRAM

In view of the results described, a revised constitution diagram was constructed (Fig. 3). The liquidus from 0 per cent. beryllium to the eutectic is believed to be accurate, but beyond the eutectic it is uncertain and is indicated by a dotted line.

The eutectic composition (0.87 per cent. beryllium) was determined by the intersection of the hypoeutectic liquidus curve with the eutectic horizontal. Moreover, microscopic examination placed the eutectic between 0.75 per cent. beryllium and 0.95 per cent. beryllium. The 0.75 per cent. sample contained many primary aluminum dendrites, and the 0.95 per cent. beryllium sample contained several particles of primary beryllium.

The eutectic temperature was placed at 645° C. by both cooling and heating curves.

The solid solubility is indicated by a dotted line because only one definite point is known—that at 631° C. as determined by the hardness tests described. Besides this point, the microscopic examinations,

the approximate solubility at room temperature, and the fact that solubility usually changes more rapidly near the eutectic temperature, have aided in sketching in this curve.

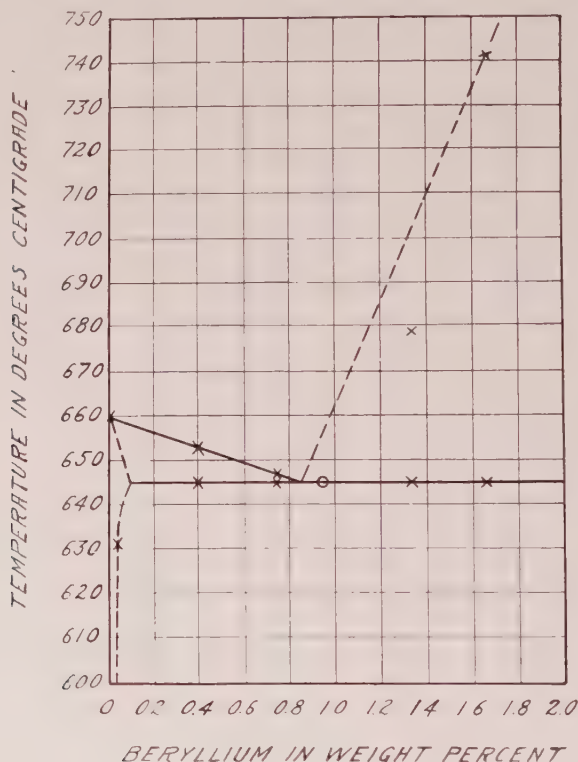


FIG. 3.—REVISED CONSTITUTION DIAGRAM.

STRUCTURE OF ALUMINUM-BERYLLIUM ALLOYS

The beryllium constituent is much harder than aluminum, and unless the particles are very small they stand out in relief after polishing. On this account, and because the beryllium constituent is of a fairly dark blue-gray color it can, in most cases, be easily recognized without any

FIG. 4a.—EUTECTIC AREA IN 1.34 PER CENT. BE CHILL-CAST AL-BE ALLOY. SAMPLE No. 4406. ETCHED WITH 5 PER CENT. HNO_3 + 1 PER CENT. HF. $\times 1000$.

FIG. 4b.—EUTECTIC AREA IN 1.34 PER CENT. BE CHILL-CAST AL-BE ALLOY. SAMPLE No. 4406. ETCHED WITH 5 PER CENT. HNO_3 + 1 PER CENT. HF. $\times 1000$.

FIG. 5.—STRUCTURE OF 0.75 PER CENT. BE CHILL-CAST AL-BE ALLOY. SAMPLE 4319. ETCHED WITH 10 PER CENT. HNO_3 + 2 PER CENT. HF. $\times 100$.

FIG. 6.—STRUCTURE OF 1.85 PER CENT. BE CHILL-CAST AL-BE ALLOY. SAMPLE 4303. NO ETCH. $\times 100$.

FIG. 7.—STRUCTURE OF 1.85 PER CENT. BE CHILL-CAST AL-BE ALLOY. SAMPLE No. 4378. ETCHED WITH 5 PER CENT. HNO_3 + 1 PER CENT. HF. $\times 500$.

FIG. 8.—STRUCTURE OF 1.85 PER CENT. BE SLOWLY COOLED AL-BE ALLOY. SAMPLE No. 4378. ETCHED WITH 5 PER CENT. HNO_3 + 1 PER CENT. HF. $\times 100$.



FIGS. 4a TO 8. (FOR CAPTIONS SEE PAGE 628.)

etching. When the particles are very fine, as in a chill-cast eutectic, or in heat-treated samples which are near the solid-solubility curve, an alternate etching with 0.5 per cent. HF and light polishing on the last cloth uncovers beryllium particles over which aluminum has been flowed in polishing. One etch with 5 per cent. HNO_3 + 1 per cent. HF will accomplish the same purpose, but attacks and darkens the constituent considerably. The latter method is, however, satisfactory for most purposes, is quicker, and gives better contrast in photomicrographs.

The eutectic aluminum-beryllium alloy consists of colonies of needles which are very much like those of the aluminum-iron eutectic.¹⁰ This structure is shown in Figs. 4a and 4b. The size of the needles increases with the solidification time but the eutectic has the same form whether chill cast, sand cast, or slowly cooled.

In hypoeutectic alloys, the structure consists of aluminum dendrites surrounded by eutectic. Fig. 5 shows the structure of a chill-cast hypoeutectic alloy at 100 dia. magnification. As can be seen at higher magnification, the eutectic is similar in structure to that of the eutectic alloy except that the needles are shorter.

In hypereutectic alloys the structure varies with the rate of solidification. The structure of a chill-cast hypereutectic specimen, sample 4303, containing 1.85 per cent. beryllium is shown in Fig. 6. The sample was a rod of $\frac{3}{8}$ -in. dia., cast in a graphite mold having an outside diameter of 2 in. This arrangement of small rounded beryllium particles to form stars, asterisks and triangles is typical of alloys of this composition cast in graphite molds. Little if any eutectic structure can be found.

With somewhat slower solidification the structure is very different. Fig. 7 (sample 4378) shows the structure of a $\frac{1}{4}$ -in. slab which was cast in a hot iron mold.¹¹ In this are found primary beryllium, aluminum dendrites and aluminum-beryllium eutectic.

¹⁰ E. H. Dix, Jr.: A Note on the Microstructure of Aluminum-iron Alloys of High Purity. *Proc. Amer. Soc. for Test. Mat.* (1925) **25**, 2.

¹¹ No analysis was made of this sample but the intended composition was the same as 4303 and the microscopic examination of both samples in the furnace-cooled condition shows that they are very nearly of the same composition.

FIG. 9a.—STRUCTURE OF 1.85 PER CENT. BE AL-BE ALLOY ALLOWED TO SOLIDIFY IN FURNACE. SAMPLE NO. 4303. NO ETCH. $\times 100$.

FIG. 9b.—STRUCTURE OF 1.85 PER CENT. BE AL-BE ALLOY ALLOWED TO SOLIDIFY IN FURNACE. SAMPLE NO. 4303. NO ETCH. $\times 100$.

FIG. 9c.—STRUCTURE OF 1.85 PER CENT. BE AL-BE ALLOY ALLOWED TO SOLIDIFY IN FURNACE. SAMPLE NO. 4378. NO ETCH. $\times 100$.

FIG. 10a.—STRUCTURE OF CHILL-CAST 23 PER CENT. BE ALLOY. SAMPLE NO. 4403. NO ETCH. $\times 100$.

FIG. 10b.—LONGITUDINAL SECTION OF 23 PER CENT. BE SHEET. SAMPLE NO. 4403. $\times 100$.

FIG. 11a.—CHILL-CAST 0.75 PER CENT. BE AL-BE ALLOY. SAMPLE NO. 4319. ETCHED WITH 10 PER CENT. HNO_3 + 2 PER CENT. HF FOR 2 SEC. $\times 100$.



FIGS. 9a TO 11a. (FOR CAPTIONS SEE PAGE 630.)

When some of the same sample was allowed to solidify in the crucible which had been removed from the furnace, there were larger particles of primary beryllium and eutectic but no aluminum dendrites, as is shown in Fig. 8.

The structure of samples 4303 and 4378 which have been allowed to solidify in the furnace is shown in Figs. 9a, 9b, and 9c. The primary beryllium particles are generally irregular in shape, and frequently they are so arranged as to have the appearance of a large needle broken into pieces. Occasionally one of the beryllium particles will have a regular

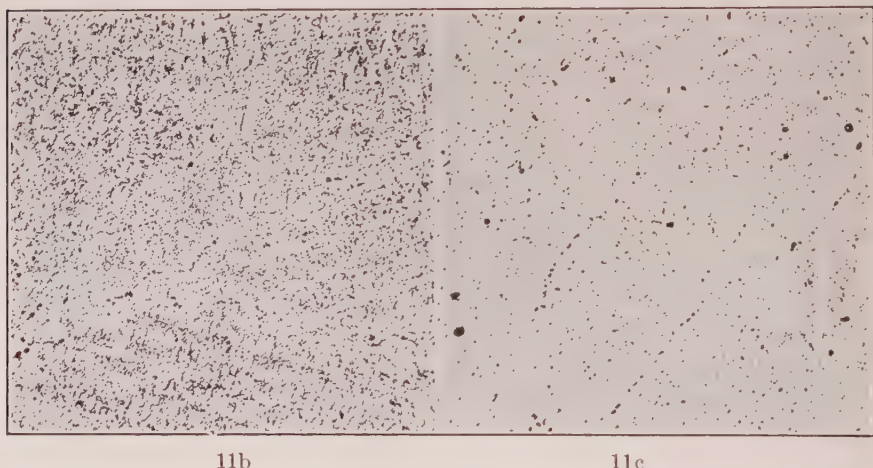


FIG. 11b.—SAME SAMPLE AS SHOWN IN FIG. 11a AFTER HEATING AT 600° C. FOR 18 HR. AND QUENCHING IN WATER. SAMPLE NO. 4319. ETCHED WITH 10 PER CENT. HNO_3 + 2 PER CENT. HF FOR 2 SEC. $\times 100$.

FIG. 11c.—SAME SAMPLE AS SHOWN IN FIG. 11a AFTER HEATING AT 600° C. FOR 24 HR. AND 637° C. FOR 18 HR. AND QUENCHING IN WATER. SAMPLE NO. 4319. ETCHED WITH 10 PER CENT. HNO_3 + 2 PER CENT. HF FOR 2 SEC. $\times 100$.

hexagonal shape. In addition to the large particles, there are many small needles and small hooked particles which have little resemblance to the eutectic structure in eutectic and hypoeutectic alloys.

The per cent. of beryllium has a pronounced effect on the structure of hypereutectic aluminum-beryllium alloys. The higher the beryllium content, the more difficult it is to develop a typical eutectic structure. In a 23 per cent. beryllium sample no eutectic could be found regardless of the cooling rate used. The highest beryllium content used in this work was 23 per cent., but Oesterheld reports a change in structure as the beryllium content is increased beyond this point. To quote from

Oosterheld's paper:¹² "In sections with a higher beryllium content, the primary beryllium constituent is easily recognized. When the temperature of the primary separation is below 900° C. the beryllium crystals have an angular form. If the primary separation takes place at 1000° C., the boundaries begin to round off, although in this case, as at lower concentrations of beryllium, there is found an arrangement of crystal branches and six pointed stars. On the other hand, when most of the crystallization takes place above 1000° C., as when the beryllium content is 71.3 atomic per cent. (45.5 weight per cent.), the rounding of the particles of constituent is complete. These relations are similar to those of the bismuth-copper system."¹³

The effect of rolling on the structure of a 23 per cent. beryllium alloy is shown in Fig. 10. A chill-cast sample (notch bar) of 4403 had the structure shown in Fig. 10a. An ingot (6 by 3 by $1\frac{3}{16}$ in.) cast in a graphite mold was rolled into sheet approximately 0.058 in. thick. In the rolling operation this sheet received 50 per cent. reduction by cold working. Fig. 10b is a longitudinal section of the sheet so produced. It will be noted that the primary beryllium particles have been elongated by the rolling although they might have been expected to be very brittle.

The effect of heat treatment on the structure of a hypoeutectic chill-cast alloy is shown in Fig. 11. Fig. 11a shows the as-cast structure — primary aluminum dendrites surrounded by eutectic. Fig. 11b shows the structure of a specimen of the same sample after holding at 600° C. for 18 hr. and quenching in water. The eutectic structure has lost its characteristic appearance, and the beryllium particles have been spheroidized by the heat treatment. There is still slight evidence of the original dendritic structure. Fig. 11c shows the structure of another specimen of the same sample which had been held at 600° C. for 24 hr., and then at 637° C. for 18 hr. and quenched in water. The beryllium particles are larger, and all indications of a dendritic structure have been lost.

Tensile and Hardness Tests of Sand Cast 0.5 Per Cent. Beryllium Alloy

Standard $\frac{1}{2}$ -in. dia. tensile test bars of sample 4347 (0.50 per cent. beryllium) were cast in sand molds. Some of the bars were given a solution heat treatment which consisted of heating at 632° C. for 30 hr. and quenching in water at room temperature. The results obtained are given in Table 7.

¹² Alloys of Beryllium with Aluminum, Copper, Silver and Iron. *Zeitschr. anorg. Chem.* (1916) **97**, 6.

¹³ G. H. J. A. Tammann: *Lehrbuch der Metallographie*. Voss, 1923, Leipzig.

TABLE 7. —*Tensile Properties and Brinell Hardness of Sand-cast 0.50 Per Cent. Beryllium Alloy*

Condition	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness 500 kg. 10-mm. Ball
As cast—immediately after casting.....	5,125	12,320	41.8	21.1
As cast—18 days after casting..		11,925	36.0	21.8
Immediately after quench (632° C.).....		13,130	32.5	23.2
Quenched and aged 3 days at room temperature.....	11,400	16,925	22.8	36.8
Quenched and aged 6 days at room temperature.....		17,050	23.5	37.4
Quenched and aged 11 days at room temperature.....		16,770	27.5	35.8

Each value is the average from two bars.

TENSILE AND HARDNESS TESTS OF FORGED 0.075 PER CENT. BERYLLIUM ALLOY

A binary aluminum-beryllium alloy containing 0.075 per cent. beryllium (sample 4386) was cast as a 4-in. square ingot, and forged into a bar approximately $\frac{5}{8}$ in. square. This bar was cut into pieces 7 in. long, some of which were used for hardness measurements and some of which were turned down into standard 0.505-in. dia. tensile test bars.

Two square bars for hardness tests and two tensile test bars were heated 20 hr. at 631° C. and quenched in ice water. The hardness results are shown in Table 8.

TABLE 8. —*Tensile and Hardness Tests of Forged 0.075 Per Cent. Be Alloy*

Condition	Hardness—500-kg. Load 100 mm. Ball, 30 Sec.
Immediately after quenching (631° C.).....	20
Quenched and aged 16 hr. at room temperature.....	31
Quenched and aged 3 days at room temperature.....	34
Quenched and aged 10 days at room temperature.....	34

After quenching and aging at room temperature for 10 days the tensile test bars gave the following results:

Bar No.	Yield Point,* Lb. per S. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.
4386-4	10,500	13,950	40.5
4386-5	10,650	14,250	36.0

* The value referred to as "yield point" is the stress which produces a total extension under load of 0.5 per cent. of the gage length.

TABLE 9.—*Tensile Tests on Aluminum-beryllium Alloy Sheet**

Sample Number	Beryllium, Per Cent.	Grade Ingot, Per Cent. Al	Condition	Yield Point	Tensile Strength	Elongation, Per Cent. in 2 In.	Brinell Hardness, 125-kg. Load, 5-mm. Ball	Scleroscope Hardness
				Lb. per Sq. In.				
4384	0	99.95	H	16,350	18,600	5.5		
4395	0.013	99.95	H	17,400	19,200	2.5		
4396	0.025	99.95	H	15,500	20,200	3.0		
4397	0.05	99.95	H	15,600	18,900	2.5		
4398	0.075	99.95	H	15,850	17,950	6.0		
4384	0	99.95	O	1,500	9,125	43.2	17.2	4
4395	0.013	99.95	O	3,070	9,110	44.0		
4396	0.025	99.95	O	3,230	9,260	41.5		
4397	0.05	99.95	O	3,220	9,400	44.0		
4398	0.075	99.95	O	3,450	9,255	48.0	18.4	4
4384	0	99.95	W	2,970	6,240	19-38		
4395	0.013	99.95	W	2,840	7,290	34.5		
4396	0.025	99.95	W	4,300	8,230	23.0		
4397	0.05	99.95	W	8,420	12,160	15.0		
4398	0.075	99.95	W	10,720	14,950	22.0		
4384	0	99.95	T	2,100	6,085	29-33	16.1	3
4395	0.013	99.95	T	3,490	7,450	19-32		
4396	0.025	99.95	T	5,500	8,980	24		
4397	0.05	99.95	T	9,530	12,370	16		
4398	0.075	99.95	T	12,050	15,395	19.5	34.7	11
4399	0	99	H	20,250	25,050	5.5		
4400	0.025	99	H	21,000	24,880	5.0		
4401	0.05	99	H	22,180	25,240	5.5		
4402	0.075	99	H	20,600	24,850	5.5		
4399	0	99	O	5,550	14,435	35.2	26.6	6
4400	0.025	99	O	4,680	13,520	37.0		
4401	0.05	99	O	5,290	14,000	34.0		
4402	0.075	99	O	4,200	13,255	35.8	24.6	6
4399	0	99	W	6,200	14,200	35.0		
4400	0.025	99	W	5,410	13,730	36.0		
4401	0.05	99	W	5,220	14,040	36.0		
4402	0.075	99	W	6,300	14,350	34.0		
4399	0	99	T	3,550	12,965	40.2	23.6	5
4400	0.025	99	T	5,370	13,890	34.0		
4401	0.05	99	T	7,400	15,270	26.0		
4402	0.075	99	T	9,000	16,835	26.7	33.9	10
4403	23.0	99.95	H	35,000	38,040	4.0	54.9	19
4403	23.0	99.95	O	16,880	26,460	12.5		
4403	23.0	99.95	W	18,630	30,160	12.5		
4403	23.0	99.95	T	24,250	33,425	11.8	53.4	17

Each value is the average of two or three tests.

H = As rolled; 50 per cent. reduction by cold working.

O = Annealed by heating to 300° C. and cooling with furnace.

W = Heated at 620° C., quenched in water, and tested immediately.

T = Heated at 620° C., quenched in water, and aged nine weeks before testing.

* All specimens were 14 gage (Brown & Sharpe).

TENSILE AND HARDNESS TESTS OF ALUMINUM-BERYLLIUM ALLOY SHEET

Alloys were made containing various amounts of beryllium and using 99.95 per cent. aluminum for one series and 99 per cent. aluminum for the other. They were cast in a graphite mold into ingots approximately 6 by 4 by $1\frac{3}{16}$ in. About 1 in. was then cropped from the top of the ingots and the remaining pieces were rolled into No. 14 gage (B. & S.) sheet on the experimental mill in the Metallurgical Laboratory of the Aluminum Company of America at New Kensington, under the direction of E. H. Dix, Jr. The reduction by cold working was 50 per cent. Tensile test specimens cut in the direction of rolling were machined and returned for heat treatment.

In Table 9, giving the tensile and hardness results, the condition of the alloy is given by the symbols H, O, W, and T. The samples marked H were tested in the as-rolled condition (50 per cent. reduction by cold working). Samples marked O were annealed by holding at 300° C. (572° F.) over night and cooling with the furnace. Specimens marked W were heat treated and tested immediately after quenching in water at room temperature. The heat treatment was at 620° C. for 1.5 hr. except for samples 4400 and 4401, which were held at 600° C. for 15 hr. and then at 620° C. for 1 hr. The specimens marked T were heat treated at the same time as the specimens marked W, but were allowed to age at room temperature for approximately nine weeks before testing.

DENSITY OF ALUMINUM-BERYLLIUM ALLOYS

The densities of some aluminum-beryllium alloys were calculated on the assumption that the densities of the elements remain the same after alloying, and the results are given in Fig. 12. This assumption has been found to give a very close approximation for many alloys.

Density measurements were made at New Kensington, by C. S. Taylor, on three samples of aluminum-beryllium alloy sheet in the as-rolled condition (50 per cent. reduction by cold working). The

TABLE 10.—*Densities of Aluminum-beryllium Alloy Sheet*

Sample Number	Per Cent. Be by Weight	Observed Density	Calculated Density
4395	0.013	2.699	
4398	0.075	2.698	
4403	23.0	2.435	2.438

results are given in Table 10. It will be noted that the agreement between the observed and calculated value for the 23.0 beryllium sample

is very good. It is probable therefore that the difference between observed and calculated values would not be large at any point on the curve.

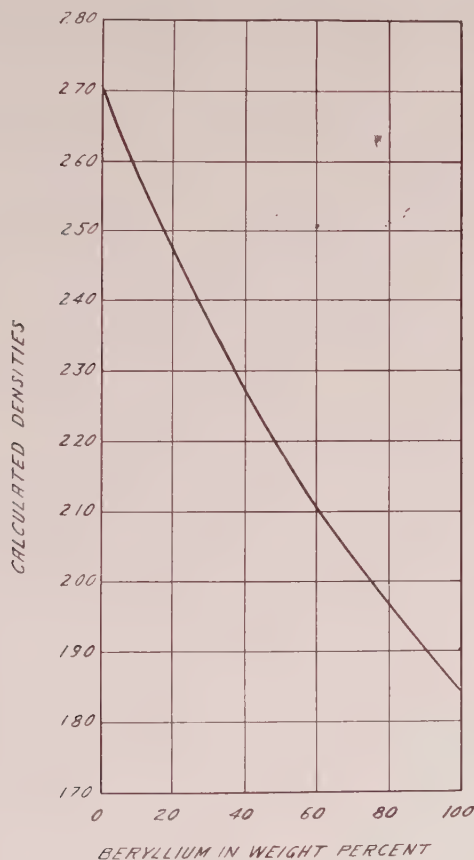


FIG. 12.—CALCULATED DENSITIES OF AL-BE ALLOYS.

ALUMINUM-BERYLLIUM-COPPER ALLOYS

Considerable work was done to determine the effect of small beryllium additions on a number of different alloys which could be age-hardened without the beryllium. In general the addition of beryllium increased the Brinell hardness of the alloys a few points—usually two to four points, sometimes as much as ten, in a few cases none. This was true of both the as-cast specimens (chill cast), and those which had been given a solution heat treatment and allowed to age at room temperature for a week or two. One exceptional case was found; that of the aluminum-beryllium-copper alloys.

A binary aluminum-copper alloy made from 99.95 per cent. aluminum ingot and cathode copper and containing 4.0 per cent. copper had a hardness of 47 when cast in an iron mold into a slab $\frac{1}{4}$ -in. thick. Upon aging at room temperature without a solution heat treatment, the hardness changed very little. The maximum reading obtained was 49 (with 8 and 16 days aging). Likewise, a sample made from 99.95 per cent. aluminum and containing 0.50 per cent. beryllium did not age-harden appreciably at room temperature without a solution heat treatment when chill cast in the same manner as the aluminum-copper alloy. The hardness immediately after casting was 25.9 and after aging at room temperature 22 days was 26.1. However, it was found that aluminum-beryllium-copper alloys containing 4.0 per cent. copper and 0.54 per cent. beryllium did age-harden considerably under the same conditions. The hardness immediately after casting was 49 and after aging 13 days at room temperature was 62. Samples of other compositions behaved in a similar manner.

Moreover, it was found that after a solution heat treatment some of the samples containing beryllium age-hardened more at room temperature than the corresponding samples without beryllium.

Three series of aluminum-beryllium-copper alloys were made and cast in an iron mold into slabs $\frac{1}{4}$ in. thick. In one series the copper was held constant at 3.0 per cent. and the beryllium contents were 0.025 per cent., 0.05 per cent., 0.125 per cent., 0.48 per cent. In another the copper was 4.0 per cent. and the beryllium 0.00 per cent., 0.05 per cent., 0.10 per cent., 0.15 per cent., 0.25 per cent., and 0.54 per cent. In the third series the copper was 5.5 per cent. and the beryllium 0.00 per cent., 0.025 per cent., 0.05 per cent., 0.075 per cent., 0.125 per cent., 0.47 per cent. Specimens of each alloy were Brinelled immediately after casting and after various periods of aging at room temperature. Other specimens of each alloy were given a solution heat treatment (at 589° C. for 3 per cent. copper series, 550° C. for 4 per cent. copper series, and 540° C. for 5.5 per cent. copper series, quenching in water at room temperature) and Brinelled immediately after quenching and after various periods of aging at room temperature. Tables 11 to 16 give the results obtained.

TABLE 11.—*Brinell Hardness of 3 Per Cent. Copper Series without Heat Treatment*

Sample.....	4380	4381	4382	4383
Beryllium, Per Cent.	0.025	0.05	0.125	0.54
Immediately after casting.....	45	48	48	44
Aged 1 day at room temperature.....	55	58	55	52
Aged 8 days at room temperature.....	60	64	60	60
Aged 19 days at room temperature.....	67	67	64	61

TABLE 12.—*Brinell Hardness of 3 Per Cent. Copper Series Quenched from 589° C.*

Sample..... Beryllium, Per Cent.....	4380 0.025	4381 0.05	4382 0.125	4383 0.54
Immediately after quenching.....	52	58	57	51
Quenched and aged 2 days at room tempera- ture.....	79	87	86	81
Quenched and aged 6 days at room tempera- ture.....	78	88	87	81
Quenched and aged 12 days at room tempera- ture.....	83	87	87	83

TABLE 13.—*Brinell Hardness of 4 Per Cent. Copper Series without Heat Treatment*

Sample..... Beryllium, Per Cent.....	4408 0	4409 0.05	4410 0.10	4411 0.15	4412 0.25	4413 0.54
Immediately after casting.....	47	55	50	50	48	49
Aged 13 days at room temperature.....				67	65	62
Aged 14 days at room temperature.....	49	69	64			

TABLE 14.—*Brinell Hardness of 4 Per Cent. Copper Series Quenched from 550° C.*

Sample..... Beryllium, Per Cent.....	4408 0	4409 0.05	4410 0.10	4411 0.15	4412 0.25	4413 0.54
Immediately after quenching.....	60	58	65	67	62	54
Quenched and aged 1 day at room temperature.....	78	78	89	90	89	83
Quenched and aged 2 days at room temperature.....	79	82	92	93	91	87
Quenched and aged 5 days at room temperature.....	82	89	91	92	91	86
Quenched and aged 12 days at room temperature.....	78	93	97	98	94	87

TABLE 15.—*Brinell Hardness of 5.5 Per Cent. Copper Series without Heat Treatment*

Sample..... Beryllium, Per Cent.....	4391 0.025	4392 0.075	4393 0.125	4394 0.47
Immediately after casting.....	64	64	64	56
After 3 days at room temperature.....	71	74	74	65
Aged 8 days at room temperature.....	73	73	76	68
Aged 15 days at room temperature.....	74	77	77	69

TABLE 16.—*Brinell Hardness of 5.5 Per Cent. Copper Series Quenched from 540° C.*

Sample.....	{ 4372 4375 }	4391	{ 4371 4376 }	4392	4393	4394
Beryllium, Per Cent.....	0	0.025	0.05	0.075	0.125	0.47
Immediately after quenching.....	76	70	70	66	65	61
Quenched and aged 1 day at room temperature.....	91	85	83	82	83	82
Quenched and aged 5 days at room temperature.....	95	88	91	87	87	88
Quenched and aged 13 days at room temperature.....	95	92	93	90	92	87

These results show that beryllium increased the hardness of the 3 per cent. copper and 4 per cent. copper alloys both with and without heat treatment. The optimum beryllium content is between 0.05 and 0.25 per cent. In the case of the heat-treated 5.5 per cent. copper alloys the beryllium was somewhat detrimental to hardness.

In order to determine the improvement in tensile properties due to beryllium permanent mold test bars of $\frac{1}{2}$ -in. dia. of the compositions shown in Table 17 were heated at 538° C. for 18 hr. and quenched in water at room temperature. They were allowed to age for two weeks and were then tested with the results shown in Table 17.

TABLE 17.—*Tensile and Hardness Tests of Chill-cast Al-Be-Cu Alloys Heat Treated at 538° C. and Aged at Room Temperature*

Sample Number	Composition, Per Cent.		Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 500-kg. Load 10-mm. Ball
	Cu	Be				
4359 ^a	4.0	0.0	22,800	38,100	12	79
4360 ^a	4.0	0.05	26,500	45,800	13	98
4381 ^b	3.0	0.05	25,400	41,600	14	83
4411 ^b	4.0	0.15	27,800	46,700	14	93
4436 ^a	3.0	0.21	25,600	42,400	14	86

^a The values given are the average of three tests.

^b The values given are the average of four tests.

Tensile and hardness tests were also made on some aluminum-beryllium-copper alloy sheet which was made as described in the section

on Tensile and Hardness Tests on Aluminum-beryllium Alloy Sheet. The results obtained are given in Table 18.

TABLE 18.—*Tensile and Hardness Tests on Aluminum-beryllium-copper Alloy Sheet**

Sample Number	Be, Per Cent.	Cu, Per Cent.	Grade Ingot, Per Cent. Al	Condition	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness, 125-kg. Load 5-mm. Ball	Sclero-scope Hardness
4339	0.81	6.0	99.95	H	33,250	37,035	3.0	66.3	25
4404	0.075	3.0	99.95	H	29,050	35,100	5.5		
4405	0.075	4.0	99.95	H	32,750	36,145	5.0	63.2	23
4339	0.81	6.0	99.95	O	8,050	19,270	25.0		
4404	0.075	3.0	99.95	O	5,950	16,820	29.2	31.0	7
4405	0.075	4.0	99.95	O	7,570	17,850	28.5		
4339	0.81	6.0	99.95	W	18,950	39,850	19.5		
4404	0.075	3.0	99.95	W	16,000	33,100	21.0		
4405	0.075	4.0	99.95	W	19,250	37,950	21.0		
4339	0.81	6.0	99.95	T	28,750	49,145	17.3	82.0	25
4404	0.075	3.0	99.95	T	26,250	42,645	20.0	77.3	23
4405	0.075	4.0	99.95	T	29,000	47,010	19.2	82.9	26

* This sheet was 14 gage rolled in such a manner that it received 50 per cent. reduction by cold working.

Each value is the average of 2 or 3 tests.

H = As rolled condition.

O = Heated at 300° C., and furnace cooled.

W = Heated at 510° C., and quenched in water, and tested immediately.

T = Heated at 510° C., quenched in water, and aged at room temperature for nine weeks before testing.

Note: For comparison, it may be mentioned that tests previously made on 14-gage sheet of an alloy containing 4.67 per cent. Cu (Fe 0.04 per cent.; Si 0.04 per cent.) showed 45,000 lb. per sq. in. tensile strength and 19.6 per cent. elongation after quenching from 510° C. and aging 116 days at room temperature.

SALT-SPRAY CORROSION TESTS OF ALUMINUM-BERYLLIUM, AND ALUMINUM-BERYLLIUM-COPPER SHEET

According to C. H. Iverson,¹⁴ an aluminum-beryllium alloy containing 2 per cent. of beryllium resisted the action of sea water perfectly. Other less definite claims have also been made for the corrosion resistance of aluminum-beryllium alloys. Moreover, preliminary qualitative corrosion tests carried out as a part of the present work seemed to show that certain heat-treated aluminum-beryllium alloys did resist salt-water corrosion very well. Consequently, salt-spray corrosion tests were carried out on sheet specimens of aluminum-beryllium and aluminum-beryllium-copper sheet specimens.

The specimens which were used for the salt-spray corrosion tests were cut in the direction of rolling from the same sheet, and heat treated

¹⁴ See Table 3.

and tested at the same time as the specimens which were used for the determination of tensile properties. For each alloy and each condition (H, O, and T)¹⁵ five specimens were tested in the corroded condition and two as controls.

TABLE 19.—*Summary of Results of Corrosion Tests on Aluminum-beryllium Alloy Sheet*

Sample Number	Composition, Per Cent. Be	Composition, Per Cent. Cu	Aluminum Ingot	Condition	Tensile Strength of Controls	Tensile Strength of Corroded Specimens	Tensile Strength, Per Cent. Change	Yield Point Controls	Yield Point Corroded Specimens	Yield Point, Per Cent. Change	Elongation Controls	Elongation Corroded Specimens	Elongation, Per Cent. Change
4384			99.95	O	9,125	8,935	- 2.08	1,500	2,450	+63.3	43.2	44.0	+ 1.85
4384			99.95	T	6,085	6,320	+ 3.86	2,100	2,300	+ 9.52	29.3	32.8	+11.9
4398	0.075		99.95	O	9,255	9,375	+ 1.30	2,800	3,450	+23.2	48.0	43.1	-10.2
4398	0.075		99.95	T	15,395	15,380	- 0.10	12,050	11,850	- 1.66	19.5	21.4	+ 9.74
4399			99	O	14,435	13,225	- 8.38	5,550	5,600	+ 0.90	35.2	17.0	-51.7
4399			99	T	12,965	11,775	- 9.18	3,550	3,350	- 5.63	40.2	16.8	-58.2
4402	0.075		99	O	13,255	12,195	- 8.00	4,200	4,150	- 1.19	35.8	14.3	-60.1
4402	0.075		99	T	16,835	15,370	- 8.70	9,000	8,900	- 1.11	26.7	10.4	-61.0
4403	23.0		99.95	H	38,040	36,335	- 4.48	35,000	34,000	- 2.86	4.0	1.63	-59.2
4403	23.0		99.95	T	31,080	33,425	+ 7.55	23,000	24,250	+ 5.43	11.0	12.3	+11.8
4404	0.075	3.0	99.95	O	16,820	15,485	- 7.04	5,950	5,600	- 5.88	29.2	16.0	-45.2
4404	0.075	3.0	99.95	T	43,645	38,865	- 8.86	26,250	26,250	0.00	20.0	13.2	-34.0
4405	0.075	4.0	99.95	H	36,145	33,380	- 7.65	32,750	31,500	- 3.82	5.00	2.25	-55.0
4405	0.075	4.0	99.95	T	47,010	41,680	-11.3	29,000	29,125	+ 0.43	19.2	9.88	-48.5
4339	0.81	6.0	99.95	H	37,035	34,510	- 6.82	33,250	32,750	- 1.50	3.0	1.13	-62.3
4339	0.81	6.0	99.95	T	49,145	44,090	-10.3	28,750	30,250	+ 5.22	17.3	8.00	-53.8
Standards of comparison			178	T	56,140	53,555	- 4.60		35,500		21.0	9.17	-56.3
			178	T	60,510	55,465	- 8.34		36,750		21.2	8.20	-61.3
			178	T	58,550	51,945	-11.3	37,750	37,000	- 2.0	18.0	6.80	-62.2

H = As rolled; 50 per cent. reduction by cold working.

O = Annealed by heating at 300° C. and cooling with furnace.

T = Heated at 620° C., quenched in water and aged at room temperature for nine weeks.

The specimens were subjected to corrosion, under the direction of E. H. Dix, Jr., in a salt-spray chamber for 1300 hr., using a spray of 20 per cent. sodium chloride solution. The air supply was off once for 44 hr. The maximum temperature was 27° C. and the minimum 14° C. The average of three readings taken daily was 22° C. The results of the corrosion tests are given in Tables 19 and 20.

It seems that beryllium does not noticeably improve the corrosion resistance of any of the alloys tested, and decreases it when the alloy is in the annealed or as-rolled condition. However, when the alloy has been given a solution heat treatment, the beryllium does not decrease the corrosion resistance, at least of 99.95 per cent. aluminum, even up to 23 per cent. beryllium. To obtain corrosion resistance at all remarkable, it would apparently be necessary to use aluminum of high purity.

¹⁵ See section on tensile properties for description of the heat treatments used.

TABLE 20.—*Surface Appearance of Specimens When Removed from Tank*

Specimen	Condition	Description
4384	O	Very light etch. No spots, etc.
4384	T	Quite heavy etch. Uniform. Shows medium grain size very plainly.
4398	T	Similar to 4384T. Slightly heavier, but uniform. Faint grain etch.
4398	O	Very similar to 4398T. No real difference.
4399	O	Heavy etch, irregular. Considerable number of pits and spots.
4399	T	General appearance like 4399-O but in much worse condition.
4402	O	Practically same as 4399T.
4402	T	Very much like 4399-O in all respects.
4403	T	Heavy etch, fairly regular.
4403	H	Fairly heavy etch, somewhat spotted.
4404	O	Very heavy, irregular attack, badly spotted. Some pits and blisters.
4404	T	Heavy, irregular etch, streaked and spotted with dark deposit.
4405	T	No real difference from 4404T.
4405	H	Very similar to 4404T, but more uniform attack over entire specimen.
4339	H	Very heavy attack with coating of corrosion product.
4339	T	Practically identical with 4404T in all respects.
M 660	T	17S specimens used as controls. Fairly heavy etch in all,
M 729	T	streaked with white corrosion product, M 729 and 1961
M 1961	T	being slightly the worse. Dark spots on all. Surface apparently much darkened in all specimens.

DISCUSSION

P. HIDNERT and W. T. SWEENEY (written discussion).—The specific gravity reported in Table 2 is equivalent to a density of 1.839 gm. per cu. cm. at 20° C. Miss E. E. Hill of the Bureau of Standards recently found the density¹⁶ of a sample of cast beryllium (98.9 per cent.) to be 1.835 gm. per cu. cm. at 20° C. These values show satisfactory agreement.

The electrical conductivity reported in the same table corresponds to an electrical resistivity of 18.5 microhm-cm. at 20° C. The electrical resistivity¹⁶ of a rod of cast beryllium (98.9 per cent.) was recently determined under the direction of Dr. F. Wenner of the Bureau of Standards, and found to be 10.1 microhm-cm. at 20° C. It is believed that the latter value is more reliable than the former.

A comparison of the composition by mixture and the composition by analysis of the five aluminum-beryllium alloys (4 to 33 per cent. Be) which were investigated¹⁶ by the Bureau of Standards, shows that the beryllium content by analysis was lower than the beryllium content by mixture. The average variation was 2.4 per cent. These results are in agreement with the general statement by Archer and Fink.

¹⁶ P. Hidnert and W. T. Sweeney: *Bur. of Stds. Sci. Paper* 565 (1927) **22**, 533.

H. S. RAWDON, Washington, D. C. (written discussion).—In connection with the investigation of the corrosion-resistance of sheet aluminum alloys of the duralumin type which has been in progress at the Bureau of Standards for the last 2½ years, a little consideration was given to aluminum alloys containing beryllium. Two alloys were prepared, the composition of which was chosen on the basis of the results reported by Kroll¹⁷ and of the suggestions given by Corson concerning the possible use of beryllium in aluminum alloys.¹⁸

Two alloys representative of the two general series given by Kroll—that is, the magnesium-beryllide and the beryllium-silicide series—were prepared, the compositions chosen being approximately those which have given the best results in Kroll's work. Corson's conclusion that very little, if any, improvement of aluminum alloys can be expected from the simple addition of beryllium but that perhaps beryllium can be used advantageously as a hardener by forming a silicide, Be_2Si , as magnesium is, is in general agreement with Kroll's results.

No difficulty was experienced in the addition of the beryllium in making the alloys; this was done in the high-frequency induction furnace, without flux. The aluminum was heated to a rather high temperature, 1300° C. approximately, and the beryllium then inserted on the end of a graphite rod. The other additions, magnesium and silicon, were made in the same manner at lower temperatures (800° C. for magnesium and 1250° C. for silicon). The compositions of the two alloys prepared are given in Table 21. It will be noted that the loss of beryllium was not excessive, considering that no special precautions had been taken to prevent it.

TABLE 21.—*Composition of Aluminum Alloys Containing Beryllium*^a

Element Determined	Alloy No. 974 (Magnesium-beryllide type)		Alloy No. 975 (Beryllium-silicide Type)	
	Intended Composition, Per Cent.	Analysis Per Cent.	Intended Composition, Per Cent.	Analysis, Per Cent.
Cu.....		0.05		0.05
Si.....		0.14	0.8	0.8
Be.....	1	0.8	0.5	0.4
Fe.....		0.09		0.08
Mg.....	1	1.2		
Ca {		not detected		not detected
Mn {				
Al.....	98	97.72 diff.	98.7	98.67 diff.

^a Analyses by J. A. Scherrer, Chemist, Bureau of Standards. Since alloy 974 contains an appreciable amount of silicon (0.14 per cent.), considerable magnesium silicide may be formed. The properties of this alloy cannot be attributed, entirely, therefore to the magnesium beryllide present.

No difficulty was experienced in rolling these alloys into strip form, the work being done under the supervision of J. R. Freeman, Jr., in the experimental rolling mill at the Bureau of Standards. The material was rolled to 14-gage thickness. Longitudinal tension specimens were cut from these strips for the following tests.

Preliminary tests showed that the heat treatment commonly used for sheet duralumin (quenching in cold water from 500 to 510° C., aging at room temperature)

¹⁷ W. Kroll: Vergütbare Aluminium Legierungen. *Metall und Erz* (1926) **14**, 613.

¹⁸ M. G. Corson: Aluminum; the Metal and Its Alloys, 280. 1926.

produced no appreciable hardening of either of the alloys and a series of Brinell tests on small samples quenched from increasingly higher temperatures and aged at elevated temperatures confirmed the conclusions of Kroll that the quenching should be done from a temperature just below the eutectic temperature and followed by accelerated aging. The tensile properties of the alloys in the annealed and heat-treated conditions are summarized in Table 22.

TABLE 22.—*Tensile Properties of Aluminum Alloys Containing Beryllium*

Treatment Number	Alloy Number	Heat Treatment	Tensile Properties	
			Ultimate Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
1	974	15 min. at 500° C., quenched in cold water. Annealed 2 hr., 350° C. ^a	23,400	26
2	974	15 min. at 550° C., quenched in cold water ^b	28,300	20
3	974	15 min., 600° C., quenched in cold water ^b	29,300	18
1	975	15 min., 500° C., quenched in cold water. Annealed 2 hr., 350° C. ^a	17,600	27.0
2	975	15 min. at 550° C., quenched in cold water ^b	21,400	17.5
3	975	15 min., 600° C., quenched in cold water ^b	28,500	11.5 ^c

^a Aged at room temperature.

^b Aged 48 hr. at 150° C.

^c Broke outside central 2-in. gage length

It will be noted that by the high-temperature treatment, the degree of hardening of the alloy of the beryllium silicide type (No. 975) was very considerably higher than for the alloy of the other type (magnesium beryllide).

The behavior of the materials when subjected to severe corrosive conditions was determined by corroding full-size tension bars by the intermittent-immersion method (15-min. intervals) in a solution consisting of nine parts (by volume) of a normal solution of sodium chloride and one part of commercial hydrogen peroxide. The tensile properties of the corroded bars are then determined. In the Bureau of Standards investigation referred to above, it has been found that sheet aluminum alloys of the duralumin type are, as a rule, severely attacked by this solution, and the tensile properties correspondingly lowered, the lowering of the elongation being more marked, however, than that of the ultimate tensile strength. The mode of attack is largely intercrystalline in character and as a rule is most pronounced if much copper is present in the alloy. The results obtained with the beryllium alloys when tested in this manner are summarized in Table 23.

Details concerning the behavior of alloys of the duralumin type when tested in this same manner need not be given here. The results given by the authors in Table 19 for the alloy 17S are quite representative. The results in Table 3 show clearly that, for these two particular Al-Be alloys, the degree of corrosion resistance against oxidizing chloride solutions is very much better than is that of the duralumin type of alloy.

TABLE 23.—*Tensile Properties of Aluminum-beryllium Alloys after Corrosion by Intermittent Immersion^a*

Alloy Number	Treatment ^b	Corrosion Period, Days	Tensile Properties	
			Ultimate Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.
974	2	0	28,300	20
		4½	27,700	15.5
		7½	27,700	15.5
		12	27,900	14.
975	2	0	21,400	17.5
		7½	21,500	12.5
		12	21,100	16.5
974	3	0	29,300	18.
		4½	29,200	18.5
		7½	29,300	14.0
		12	27,700	11.5
975	3	0	28,500	11.5
		4½	29,300	10.5
		7½	28,300	11.5
		12	28,300	11.0

^a Immersion at 15-min. intervals in a solution of sodium chloride (9 parts by volume of a normal solution) and hydrogen peroxide (1 part commercial solution).

^b See Table 22.

The most interesting observation made on these alloys was the fact that no trace of intercrystalline attack was shown by either even after prolonged corrosion (12 days in the oxidizing chloride solution). On account of the inferior tensile properties of these alloys, as compared with the duralumin type, these materials are not to be considered seriously for replacing the latter. Their superior corrosion resistance, however, should be borne in mind and possibly alloys of this type may serve a useful purpose to meet some unusual conditions.

It may also be of interest to mention some preliminary data on the modulus of elasticity in compression of commercial beryllium and aluminum-beryllium alloy of approximately 33 per cent. Be, determined on cast specimens by J. R. Freeman, Jr. The commercial beryllium had a modulus of approximately 27,500,000 lb. per sq. in. and the alloy one of approximately 14,000,000 lb. per sq. in. The small size of the specimens made testing difficult and the figures are subject to revision when more suitable specimens can be obtained. The data indicate that the modulus is high, but not so high as has been calculated from theoretical considerations alone.

R. S. ARCHER and W. L. FINK (written discussion).—It is gratifying to the authors that so much unpublished information has been contributed in the discussions; the corrosion data are particularly interesting. The authors are also pleased that attention has been called to the more accurate determination of the electrical resistivity of beryllium.

Behavior of Molybdenum as Resistor in the Electric Furnace

BY HENRY J. MILLER* AND MARCELLA LINDEMAN,* CLEVELAND, OHIO

(New York Meeting, February, 1929)

DURING some experiments made by Henry J. Miller, partly in Germany and partly in the United States, in which it was found necessary to melt metals in quantities up to 60 kg. in a vacuum or under low pressures of hydrogen, molybdenum was tried as the resistor in the electric melting furnaces. Molybdenum ribbons 16 by 0.55 mm. and 18 by 0.45 mm. were used as resistors. The furnaces were of the type shown in Fig. 1.

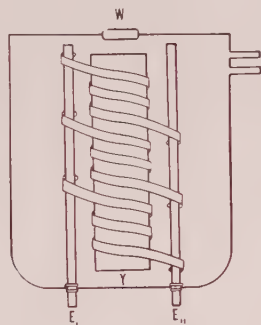


FIG. 1.—TYPE OF FURNACE USED.

About the heating tube, Y , are wound parallel resistors of molybdenum ribbon from the water-cooled electrodes, E_1 , E_2 . The whole is within a copper container having outlets for the removal or introduction of gases and a window, W , for observation, the space about the heating tube and electrodes being filled with insulating material.

The life of the molybdenum used as the resistor was found to depend very much on the manner of using it, its failure being due in some cases to thinning by evaporation or chemical reaction and in others to hardening, which prevented it from following the expansions and shrinking of the heating tubing without cracking. As such failures are often rather expensive in commercial work, it was thought worth while to determine the causes.

The factors influencing the behavior of molybdenum resistors used in this manner may be briefly stated as follows:

* Research Laboratory, Incandescent Lamp Dept., General Electric Co.

1. Initial condition of molybdenum

Chemical purity

Process of manufacture, with regard to mechanical and heat treatment

2. Temperature and time of aging in furnace

3. Heating tubing—kind of tube on which resistor is wound

4. Heat insulation

5. Gases present in furnace

METHODS OF PRODUCING MOLYBDENUM RESISTORS

There are two ways of producing molybdenum ribbon or wire suitable for resistors in vacuum furnaces: (1) Molybdenum oxide or other suitable molybdenum compounds in powder form may be reduced to metallic molybdenum, then pressed, swaged and rolled or drawn; (2) particles, each consisting of molybdenum and oxygen, may be pressed together and the pressed body may be reduced to metallic molybdenum. It can not be stated definitely whether these particles composed of molybdenum and oxygen are in the form of a chemical compound, of a solid solution, or of molybdenum with occluded or adsorbed oxygen.

The first process, with some modifications, is covered by a large group of patents, while the second is described in the German patent¹ as "a process for the production of bodies consisting of tungsten, molybdenum, or similar refractory metals which can be directly subjected to mechanical working."

The structure of the German molybdenum ribbon produced by reducing pressed molybdenum oxide is shown in Figs. 2 and 3, in which the elongation of the grains by working may be seen, as well as the presence of a certain amount of unreduced oxide appearing as granules at the grain boundaries.

Fig. 4 shows the structure of American sheet molybdenum produced by the swaging process, from the General Electric Co. laboratories. The molybdenum ribbon used as resistors in the present work was of the German type.

MATERIAL USED FOR INSULATION AND TUBING

The heat-insulating material has been used in grain sizes from approximately 0.5 to 1.5 mm. diameter, its chemical characteristics being as follows:

1. Alumina fused in the electric arc, and sometimes subsequently freed of contaminations by treatment with hot hydrochloric acid.

2. Alumina containing as the only contamination small traces of silica was prepared by calcining pure alumina, using some gelatinous

¹ German Patent D. R. P. No. 315930, Kl40a of April 16, 1912. Dr.-Ing. Paul Schwarzkopf in Charlottenberg and Dr. S. Burgstaller in Berlin-Schöneberg.

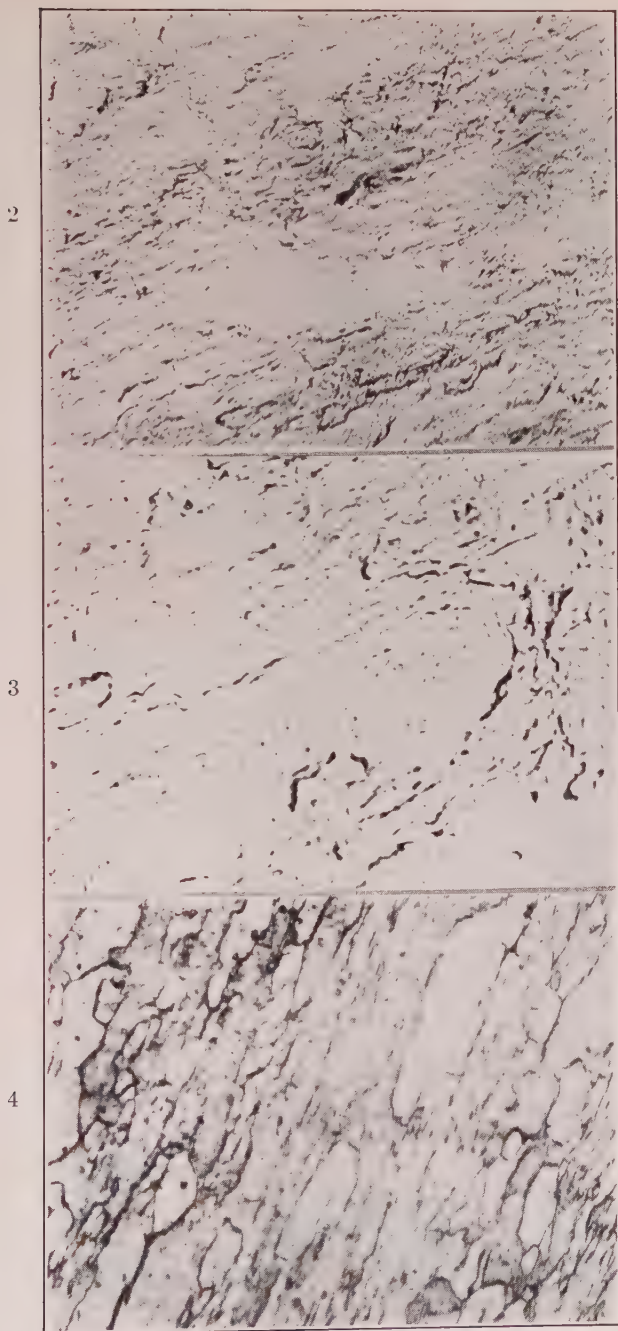


FIG. 2.—GERMAN MOLYBDENUM RIBBON, LONGITUDINAL SECTION, $\times 575$. FINE-GRAINED STRUCTURE DUE TO OXIDE PARTICLES.

FIG. 3.—GERMAN MOLYBDENUM RIBBON, LONGITUDINAL SECTION, $\times 1500$. NOTE INCLUSION OF SMALL OXIDE GRAINS.

FIG. 4.—SWAGED SHEET MOLYBDENUM FROM GENERAL ELECTRIC Co. $\times 575$.
(Figs. 2, 3 and 4 reduced to $\frac{3}{4}$ original size.)

carbon-free material as a binding agent, firing to approximately 1500° C. and subsequently crushing to the desired grain size. The calcined alumina used as raw material showed the following composition: Al_2O_3 approximately 98 per cent.; SiO_2 approximately 0.20 to 0.30 per cent.; Fe_2O_3 approximately 0.10 per cent.; Na_2O up to approximately 1.8 per cent.

3. Mixtures of 30 per cent., by weight, of Zettlitz unfired kaolin with 70 per cent. coarse fused alumina, grade 80.

4. Mixtures corresponding, as far as composition is concerned, to the "Marquardt" formula but lower in silica and containing a larger amount of previously fired material (65 per cent. fired kaolin + 35 per cent. alumina). Fusing point about 1900° C.

5. Magnesite (mostly Kärnthen magnesite).

The heating-tube materials were:

1. "Marquardt" compositions described above in No. 4.

2. Fused alumina with 30 per cent. kaolin. Fusing point about 2000° C.

3. Calcined alumina fired, with aluminum hydroxide as binder. Fusing point about 2000° C.

4. Magnesite.

The effect on the molybdenum of heating in the presence of these materials may be seen in Table 1.

TABLE 1.—*Effect on Molybdenum of Heating in Presence of Various Materials*

Insulation	Temperature, Deg. C.	Gas Condition	Condition of Molybdenum after Heating
Calcined alumina fired with aluminum hydroxide.	1920 up to melting point of Mo	Vacuum	Ductile
Calcined alumina fired with aluminum hydroxide.....	"	Hydrogen	Ductile
Pure fused alumina.....	"	Vacuum	Ductile
Pure fused alumina.....	"	Hydrogen	Ductile
Ordinary fused alumina.....	"	Vacuum	Ductile
Ordinary fused alumina.....	"	Hydrogen	Ductile
Marquardt I (low in silica).....	"	Vacuum	Ductile, eaten in spots
Marquardt I (low in silica).....	"	Hydrogen	Ductile
Marquardt II (high in silica).....	"	Vacuum	Eaten up
Marquardt II (high in silica).....	"	Hydrogen	Ductile
Alumina + 30 per cent. kaolin.....	"	Vacuum	Eaten up
Alumina + 30 per cent. kaolin.....	"	Hydrogen	Eaten up
Magnesite.....	"	Vacuum	Hardened
Magnesite.....	"	Hydrogen	Hardened

The most satisfactory material for use both as heating tubing and heat insulation was found to be calcined pure alumina, mixed with aluminum hydroxide as a binder, and fired at about 1500° C. Pure fused alumina was also found to be satisfactory. All other materials used as heat insulation sintered about the ribbons, thus constraining them to move with the working of the heating tubing and increasing the chances of cracking the resistor.

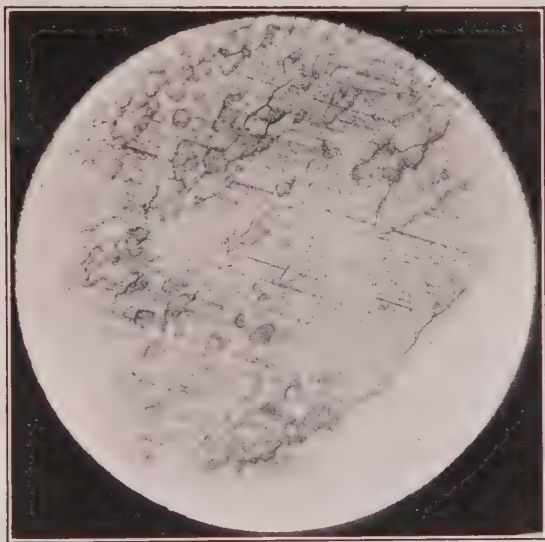


FIG. 5.—OBLIQUE SECTION OF VERY DUCTILE RIBBON HAVING LONGEST LIFE, $\times 100$. LARGE GRAINS NEAR SURFACE; SMALL GRAINS NEAR CENTRAL PORTION. (Reduced to $\frac{3}{4}$ original size.)

In all cases where the alumina was uncontaminated by silica, the molybdenum ribbon could be heated almost to its melting point and still remain ductile, or even acquire more than its initial ductility. In nearly all of these cases the surface of the ribbon appeared very bright and silvery. This silvery deposit also penetrated into the insulating material, the depth of penetration depending on its grain size and increasing with the fineness of the grain. This deposit was formed at about 1300° C.

DUCTILITY OF RESISTOR AFTER HEATING

The surfaces of these ribbons after heating have much greater ductility, in general, than the central part.² In studying their microstruc-

²The classification of hardness as given in this paper is derived from bending the molybdenum ribbon in an angle of 90° at room temperatures. "Ductile" ribbons stood one or several of these bendings, "Hard ribbons" cracked on the first bending. "Hard and brittle" ribbons cracked at the first bending and broke at the same time into small fractures in places removed from the line of bending.

ture, it was found in all cases that great ductility was accompanied by fairly large grain size, and the ribbons having greater surface ductility possessed a surface layer of plate-like crystals sometimes about ten times the size of the average crystal on the interior. This difference may be clearly seen in Fig. 5, which shows an oblique section of the ribbon. Fig. 6 shows a transverse section of one of these ribbons at the boundary between the surface layer and interior. It is believed that this ductile surface layer, as well as the deposit found on the insulation, is formed by the oxidation and subsequent reduction at higher temperatures of the molybdenum, probably caused by the presence of traces of water vapor when the furnaces are operated *in vacuo*, or by reaction with the insulating material, and later with hydrogen when that is present.

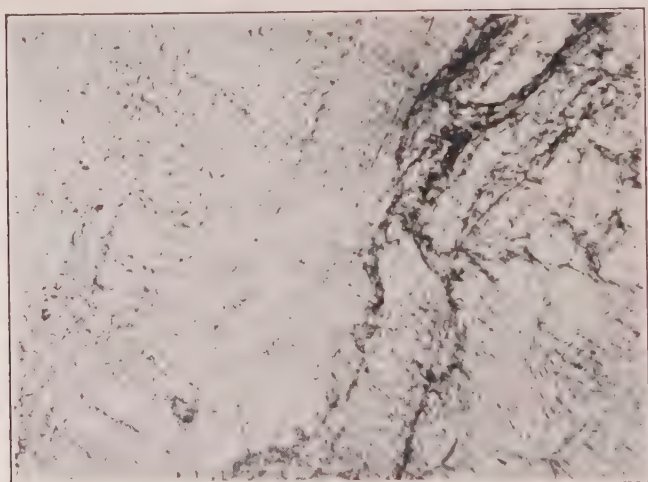


FIG. 6.—TRANSVERSE SECTION OF VERY DUCTILE RIBBON HAVING LONGEST LIFE, $\times 575$. LARGE GRAIN, SHOWN IN PART AT LEFT SIDE ON SURFACE OF RIBBON, SMALLER GRAINS AT RIGHT TOWARD INTERIOR.
(Reduced to $\frac{3}{4}$ original size.)

Ribbons having great ductility were always found to have long life, the specimen shown in Fig. 6 being used 36 times in a furnace of 10-kg. capacity.

In general, metals having small grains possess greater ductility than those having large grains, but the apparently anomalous behavior of the specimens discussed in this paper may be explained by the fact that the smaller grain size is caused by the presence of a brittle material at the grain boundaries. This was shown in a very striking manner in the samples where the ribbons were heated in a coarse-grained mixture of fused alumina and kaolin. Here regions of large crystals formed next the alumina particles alternated with regions of crystals about one-sixth their size formed near particles of kaolin.

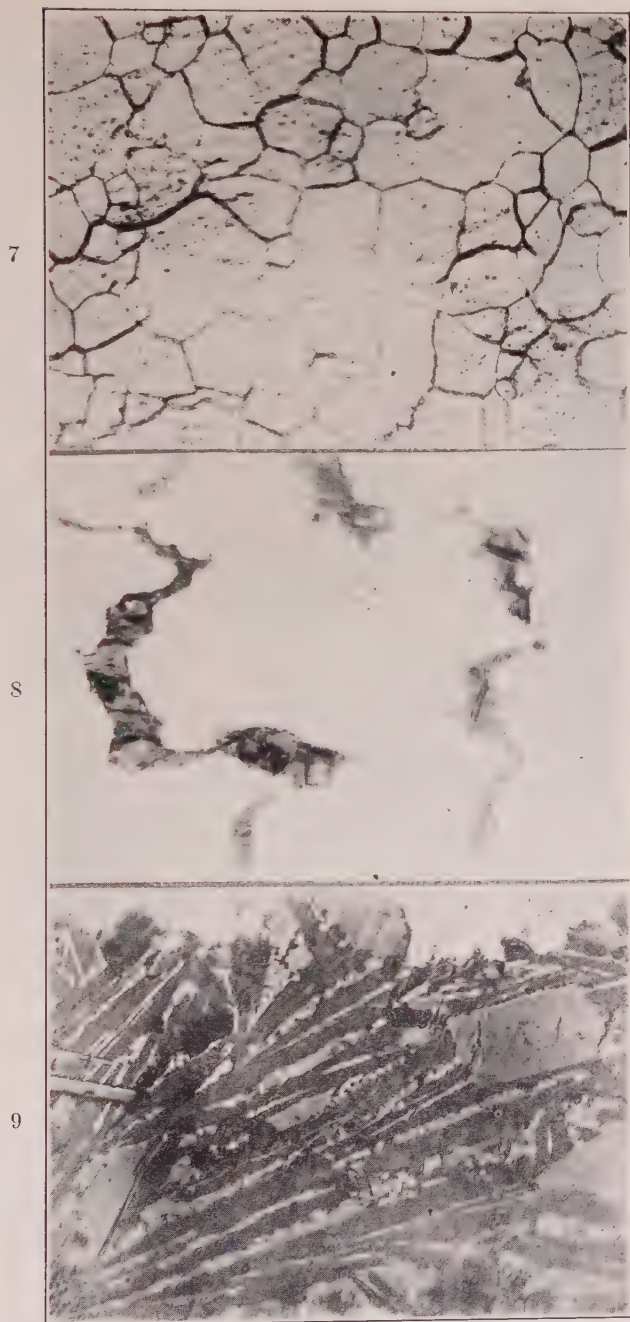


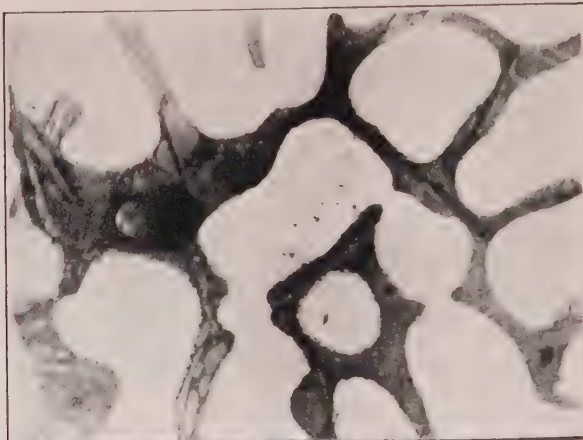
FIG. 7.—LONGITUDINAL SECTION OF VERY BRITTLE RIBBON HAVING SHORTEST LIFE, $\times 575$. SMALL GRAIN SIZE AND BRITTLINESS DUE TO INCLUSIONS OF SILICIDE AT GRAIN BOUNDARIES, SHOWING AS DARK BANDS.

FIG. 8.—SECTION OF BUCKLED PORTION OF RIBBON, $\times 280$. NOTE LARGE INCLUSIONS OF SILICIDE.

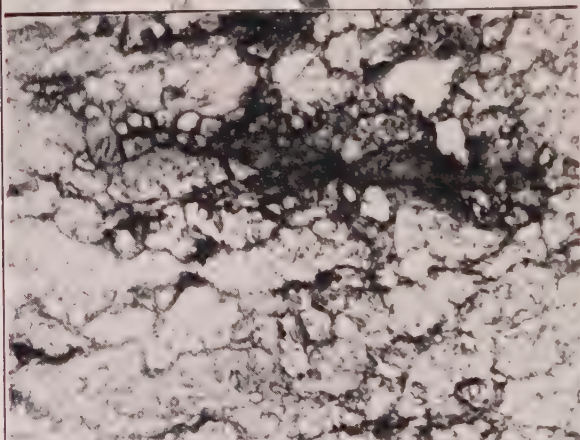
FIG. 9.—SECTION OF BUCKLED AND CRACKED PORTION OF RIBBON, $\times 280$. NOTE INCREASING AMOUNT OF SILICIDE, ONE PORTION SHOWING DOUBLE COMPOSITION, PROBABLY SILICIDE AND SILICATE.

(Figs. 7, 8 and 9 reduced to $\frac{3}{4}$ original size.)

10



11



12



FIG. 10. SECTION NEAR WHERE RIBBON WAS EATEN AWAY, $\times 280$. NOTE LARGE AMOUNT OF SILICIDE AND SILICATE.

FIG. 11.—LONGITUDINAL SECTION OF RIBBON USED IN FURNACE WITH MAGNESITE HEATING TUBING AND INSULATION, $\times 575$. SMALL GRAIN SIZE AND BRITTLINESS DUE TO FORMATION OF CARBIDES, WHICH SHOW AS SMALL BRIGHT GRAINS.

FIG. 12.—UNTREATED SURFACE OF RIBBON AFTER USE IN FURNACE, $\times 400$. NOTE DEEP HEAT-ETCHING ON GRAIN AT RIGHT, SHOWING CRYSTAL PLANES. ABSENCE OF ETCHING ON GRAIN AT LEFT DUE TO GLASSY DEPOSIT FORMED OVER IT. THIS RIBBON POSSESSED DUCTILE SURFACE LAYER. COMPARE SURFACE GRAIN SIZE WITH THAT IN FIGS. 6, 7 AND 8.

(Figs. 10, 11 and 12 reduced to $\frac{3}{4}$ original size.)

EFFECT OF SILICA, CARBON AND IMPURITIES

A very small percentage of silica is sufficient to change markedly the behavior of the resistor ribbons. Insulating material of alumina powdered in a ball-mill was used in one experiment. In this case the ribbon became very hard and brittle. When the same material was used again with new ribbon, the hardening was less pronounced, and after the fifth or sixth time it was used with new ribbons, the ribbons ceased to become hardened, due to the exhaustion of the silica by previous reactions.

It may be seen from Table 1 that increasing percentage of silica has a destructive effect, first hardening the ribbons, then causing buckling and cracking, and finally corroding them. This is probably due to the formation of molybdenum compounds or alloys containing silica or silicon as a constituent.

Figs. 7, 8, 9 and 10 show the effects of increasing amounts of silica on the structure. A section of a hardened ribbon is shown in Fig. 7, where the crystals are seen to be much smaller than in Fig. 6, having appreciable enclosures of the contaminating molybdenum-silicon compound or alloy at the grain boundaries.

When carbon is present, as in the case where magnesite³ was used, carbides are formed, which, being brittle and hard, have the same

TABLE 2.—*Effect on Molybdenum of Heating in Presence of Large Amounts of Carbon, Sulfur and Various Gases*

Materials Present	Time, Hours	Temperature, Deg. C.	Condition of Molybdenum after Heating
14 parts calcined alumina, 1 part carbon.....		1920	Hard and brittle
Powdered carbon.....		1000	Hard and brittle
Carbon monoxide.....	2	600-700	Hard
Hydrocarbons.....	2	600-700	Hard
Water gas.....	2	600-700	Ductile
Sulfur.....	3	600	No change
Sulfur dioxide.....	2	600-700	No change
Red phosphorus.....	6	600-700	Hard
Water vapor.....	1	1000	No change
Nitrogen taken from commercial tanks, having traces of oxygen...	2	600-700	Hard
Same nitrogen, oxygen removed....	2	600-700	Ductile
Molybdic acid vapor.....	2	1050	Previously hardened ribbon made ductile

³Sintered magnesite as well as fused magnesite were fired in a granular carbon furnace. The fused magnesite as well as the sintered magnesite apparently contained the carbon in form of colloidal dispersion, coloring the magnesite appreciably and in such a way that the color effect could not be ascribed to iron oxide alone.

effect as the silica compounds. These may be seen in Fig. 11 as enclosures of very high reflectivity.

Even where other materials are used there is great likelihood of carbon being present as an impurity, most of these insulators being made by

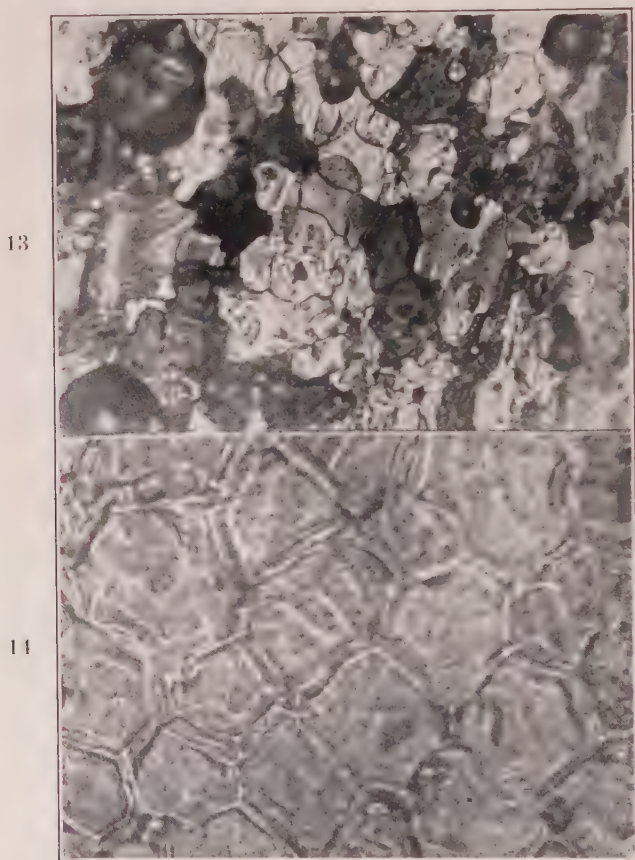


FIG. 13.—UNTREATED SURFACE, AFTER USE IN FURNACE, $\times 400$. GRAINS HEAT ETCHED, SHOWING BOUNDARIES. DIFFERENCE IN REFLECTIVITY CAUSED BY DIFFERING THICKNESSES OF OXIDE DEPOSITS, THE DEPOSITION BEING SELECTIVE AND DEPENDING ON ORIENTATION OF CRYSTALLITES.

FIG. 14.—UNTREATED SURFACE, AFTER USE IN FURNACE, $\times 400$. SAMPLE VERY BRITTLE AND HARD. (COMPARE GRAIN SIZE WITH THAT IN FIG. 12.) GRAINS OVERLAID WITH GLASSY DEPOSIT HAVING GRAIN SIZE COMPARABLE WITH THAT OF UNDERLYING MOLYBDENUM. NOTE DOUBLE NETWORK OF GRAIN BOUNDARIES.

(Figs. 13 and 14 reduced to $\frac{3}{4}$ original size.)

carbon-arc or carbon-furnace processes. Sulfur may occur in the molybdenum as an impurity, since most molybdenum is produced from sulfide ores, also traces of iron and metals similar to molybdenum, such as tungsten, vanadium, titanium, zirconium, tantalum and columbium,

which may not have been removed. It is not thought probable, however, that the presence of these impurities would tend, upon aging, to change to any great extent the properties of the molybdenum.

To test the effects produced by carbon, sulfur and gases occurring as impurities in the furnace, a series of experiments was performed in which molybdenum ribbon was heated in the presence of large amounts of these materials. The results are shown in Table 2.

SURFACE PHENOMENA FOLLOWING EXPERIMENTS

All these ribbons were found to be heat-etched in a very pronounced manner and covered with deposits of molybdenum oxides and glass

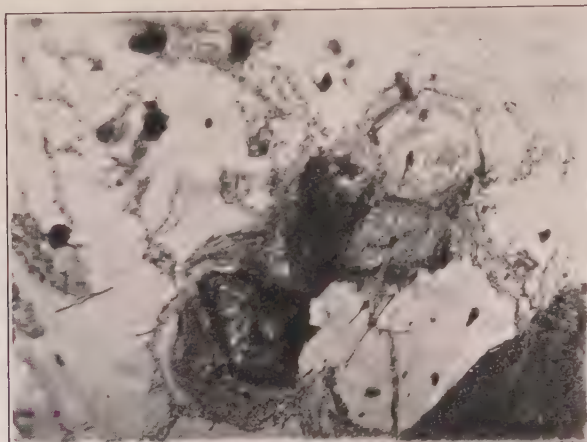


FIG. 15.—UNTREATED SURFACE, AFTER USE IN FURNACE, $\times 225$. SPECIMEN RATHER DUCTILE. (COMPARE GRAIN SIZE WITH FIGS. 12 AND 14.) BRIGHT GRAIN COVERED WITH GLASSY DEPOSIT OUT OF WHICH HEXAGONAL CRYSTALS OF ALUMINA ARE FORMING. NOTE DARK RINGS INDICATING CENTERS OF REACTION. (Reduced to $\frac{3}{4}$ original size).

formed by reaction of alumina and silica with the basic oxides of molybdenum. Both heat-etching and the deposition of reaction material were found to vary to a marked degree with orientation of the crystals. In certain cases, a striated deposit of what seemed to be a eutectic having MoO_3 as one constituent covered the entire surface. In others the molybdenum crystals were covered by a second set of crystal boundaries in the overlying glassy deposit.

Good samples of heat-etching are shown in Figs. 12 and 13. None of the microscopic samples showing *surface conditions* have been ground,

16



17



18

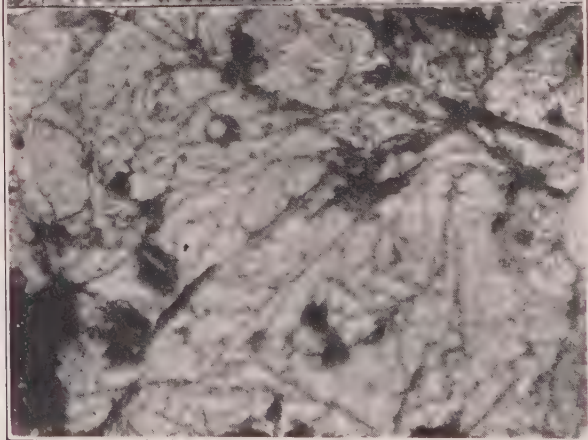


FIG. 16.—UNTREATED SURFACE AFTER USE IN FURNACE, $\times 315$. SPECIMEN VERY DUCTILE. (COMPARE GRAIN SIZE WITH FIGS. 12, 14 AND 15.) ALUMINA CRYSTALLIZING OUT OF GLASSY DEPOSIT AS IN FIG. 15.

FIG. 17.—UNTREATED SURFACE AFTER USE IN FURNACE, $\times 575$. REDDISH IRRIDESCENT LAYER OF EUTECTIC OF MoO_3 FORMED OVER SURFACE. SLIGHT INDICATIONS OF UNDERLYING GRAIN BOUNDARIES. SPECIMEN DUCTILE ON SURFACE.

FIG. 18.—UNTREATED SURFACE AFTER USE IN FURNACE, $\times 150$, SHOWING DENDRITIC DEPOSITS OF MoO_3 .

(Figs. 16, 17 and 18 reduced to $\frac{3}{4}$ original size.)

polished or etched (treated). The "natural" state of the surface is given.

In agreement with the assumption that the failure of the molybdenum ribbons used as resistors is caused by contamination of the ribbon with silica, very brittle ribbons are sometimes coated with a glass forming a crystallized *transparent* layer on the surface of the ribbons. In Fig. 14 is given a striking example of such a "glassy" surface film. The sample is taken from the hardest and most brittle ribbon ever obtained in these experiments and shows distinctly the crystal boundaries of the glass on the surface as well as the grain structure of the metal surface itself.

In Figs. 15 and 16 the chemical reaction with parts of the ceramic material used as heating tubing and heating insulator can be seen. A reaction going on at high temperature has evidently been stopped by rapid cooling and some of the products of this reaction have formed geometrically perfect crystals. Some of these are completely transparent. No other glass can be formed at the temperature of operation of the furnaces and in the presence of the materials used as ceramic parts except glass containing silica at least as a constituent (crystallization of alumina out of silica-matrix).

Fig. 17 shows a thin coating of a eutectic of MoO_3 , which appeared on a number of ribbons as a red film. Indications of the grain boundaries of the underlying molybdenum may also be seen. Dendritic surface deposits of MoO_3 are shown in Fig. 18.

CONCLUSIONS

The destruction of molybdenum ribbons used as resistors in electric furnaces is due chiefly to chemical reaction with materials present in heating tubing, insulation, or gases in the furnace. Of those materials most likely to be there, silica and carbon are the most destructive. For the best working conditions of such furnaces it is recommended that:

1. Both heating tubing and insulation should be of calcined pure alumina, mixed with aluminum hydroxide as binder and fired at 1500°C .
2. The first heating of a new furnace should be carried out under high hydrogen pressure, which may be later reduced.
3. If the material used for heating tubing or insulation contains carbon, oxides of a high degree of oxidation should be added, so that they may react with it, the products of the reaction to be removed by evacuation.
4. The molybdenum ribbon may be coated with molybdenum oxides having a low degree of oxidation to protect it from forming oxides or carbides.

Non-ferrous Secondary Metals Recovered in the United States*

BY J. P. DUNLOP,† WASHINGTON, D. C.

(New York Meeting, February, 1928)

THE fact is notable though probably little known that the United States is the only nation obtaining and distributing through its Government bureaus any data pertaining to waste metals and drosses. Some foreign governments do issue reports relating to mine or smelter production of primary metals, but none gives in scope and detail the information published now by the U. S. Bureau of Mines and formerly by the U. S. Geological Survey; and this is despite the fact that the funds annually allotted for those purposes are insignificant in comparison with allotments for the preparation of data relating to other industries of like importance.

The earliest data on the production of metals from secondary sources in the United States were contained in a press bulletin issued by the U. S. Geological Survey on Jan. 4, 1909. The information published was that for the year 1907 obtained and compiled by C. E. Siebenthal, who was one of the first to visualize the growing importance of the scrap-metal industry.

The National Conservation Commission had emphasized its opinion that the known domestic supply of certain kinds of the more important metals was being rapidly marketed and that while there was no immediate cause for concern it was best to conserve such resources. Not only had there been a lamentable lack of any data regarding the quantity of scrap metals available or used but also gross carelessness and indifference in the segregation, collection, and effective use of scrap material. Siebenthal realized that even approximately correct statistics of recoveries from the more important base-metal scrap and drosses were nearly as essential to both producers and consumers as the statistics of the output of primary metals. There were not then nor are there now sufficient funds for complete collection of data, nor was it considered the province of the Geological Survey to do more than determine approximately the recovery of secondary metals for use in supplementing those given for the primary metals. Undoubtedly the first bulletins issued did not give the full output, for it takes time to establish contacts for an inquiry covering so

* Published by permission of the Director, Bureau of Mines.

† Statistician, U. S. Bureau of Mines.

much territory and so many metals and alloys, but as the years passed the work was extended to a greater number of metals. There never has been any special effort to make the secondary metal report a technical treatise, for its purpose was primarily statistical, although considerable information was gradually added regarding methods of treating scrap metals and drosses. Excerpts from trade papers and magazines which would enable buyers and consumers of scrap to handle material properly and use it to best advantage were quoted. The Geological Survey could not answer many of the technical inquiries made, but it always endeavored to put the inquirer in touch with those who could, and moreover it always called the public attention to the vast trade in waste material and its influence on prices.

CHANGING ATTITUDE TOWARD SECONDARY METALS INDUSTRY

It was also desirable to improve the ethics of the industry and to supplement the efforts of the trade papers and associations in remedying abuses and standardizing products. It was necessary to change the public opinion that secondary materials were necessarily inferior and to remove the stigma of unfair dealing unjustly applied to dealers, collectors and sellers of waste. There were, of course, the normal percentage of crooked, grasping and unreliable dealers and smelters, but the waste-trade industry was never as bad as painted. Many good-sized fortunes had been made in the business because sellers of waste metals sadly lacked appreciation of the material they sold. Other sellers did not realize that there must be a wide margin between the price paid to them for unsegregated wastes and the price paid the dealer for sorted scrap. Because the seller could get so little for ashes, borings, filings and other waste, much of it was disposed of for the cost of removal. It is always difficult to induce a prosperous people to save, as those of Europe have done for years in apparently small matters, so the early dealers in scrap, etc., frequently did take advantage of the carelessness and ignorance of their customers. This profiteering is no longer possible to any extent, for nearly every business that has metal wastes has learned to segregate them so as to realize the most profit either by use at the plant or by sale to the highest bidder. In fact, if there is a valid criticism to make regarding the business methods of dealers in waste metals, it is that they frequently pay too much for wastes. They tend to speculate on future prices instead of relying on a normal profit on all material purchased. This practice in late years has resulted in many failures or an inadequate return for the greatly increased quantity of material handled.

Scrap material is now being handled much more efficiently at its source and much more scientifically treated at the secondary smelters that employ competent assayers and metallurgists, so that many brands

of metals and alloys approach those made from primary sources in purity and in adaptability for most purposes.

The National Association of Waste Material Dealers has aided materially in improving the ethics of the trade. It has removed much friction by its classifications of scrap and wastes and by its settlement of trade disputes by arbitration.

The U. S. Geological Survey and the Bureau of Mines have repeatedly drawn the attention of the metal trades and the public generally to the ever-growing quantity and quality of secondary materials and to the economic crime of not using them properly and fully. I regretfully admit that occasionally a flamboyant press bulletin roused the ire of the ultra-scientific in the Bureaus, but I am sure that the resultant publicity helped to banish the derision that once assailed the collector, dealer and user of waste material. Casual examination of the advertisements in a magazine devoted to waste material will enable any one to realize the scope of a trade very diversified in metals and many other lines and one of immense volume, value and uses.

STATISTICS

In the bulletin issued for 1907, the secondary recoveries of copper (including that in alloys other than brass), lead, zinc and tin were given. The aggregate quantity in tons was 77,658, and the value was \$17,196,436.

In 1909, the inquiry was extended to remelted brass and secondary antimony. The total recovery was 135,184 tons, valued at \$23,239,610. The secondary recoveries of aluminum were first compiled for 1913 and those for nickel for 1916.

The value of secondary metals recovered in 1917 was more than \$295,800,000, a record value due mainly to the high prices for metals. This value was \$21,000,000 greater than that for 1926, when the aggregate quantity of metals recovered was 1,016,880 tons, compared with 650,418 tons in 1917.

Since 1921, when the output of both primary and secondary metals was the smallest in many years, the total quantity of most secondary metals recovered has steadily increased.

Table 1 gives the secondary recoveries of certain metals and alloys and the total value from 1910-1926, by years. In addition, the yearly separate chapters issued by the Bureau of Mines now give:

The latest standard classification of old metals.

A review of the secondary metal industry.

Prices of some scrap metals and alloys.

The secondary recoveries of gold, silver and platinum.

More specific and comprehensive data and references to new methods are given under sections devoted to each metal. The nature of such information is outlined as briefly as possible.

TABLE 1.—Recorded Recovery of Certain Classes of Secondary Metals in the United States, 1910–1926, in Short Tons

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919
Copper, (including that in alloys other than brass).....	51,000	50,815	66,411	66,980	58,556	99,937	140,000	159,400	122,510	
Scrap brass remelted.....	62,000	80,370	101,523	99,315	99,038	137,500	300,000	320,000	328,800	
Lead as metal.....	29,492	30,266	33,104	33,104	29,337	36,400	56,700	45,100	41,146	
Lead in alloys.....	25,930	26,895	36,902	39,730	31,725	42,500	39,600	45,400	55,954	
Zinc as metal.....	41,223	40,513	52,251	50,005	42,969	52,900	50,700	31,400	27,108	
Zinc in alloys other than brass ¹	3,223	3,912	3,912	3,743	4,800	5,300	2,600	4,800	11,082	
Tin as metal.....	7,217	7,749	8,333	6,415	4,535	5,250	7,600	6,000	7,142	
Tin in alloys and chemical compounds.....	6,686	6,927	7,063	7,763	7,912	8,400	9,800	13,400	16,695	
Antimony as metal.....	9	10	13	45	1	2	80	6	43	
Antimony in alloys.....	2,770	2,359	2,463	2,660	2,645	3,100	4,400	4,555	5,183	
Aluminum as metal.....				2,198	2,791	5,700	12,900	6,660	6050	
Aluminum in alloys.....				2,456	1,731	2,800	6,400	9,440	9,000	
Nickel as metal.....						16	16	60	178	
Nickel in non-ferrous alloys and salts.....						800	800	800	1,215	
Total quantity.....	229,036	246,310	300,202	314,114	285,151	399,789	631,596	650,421	632,106	
Total value.....	\$45,525,500	\$52,585,390	\$77,395,843	\$72,786,027	\$57,039,706	\$114,304,430	\$265,377,556	\$295,854,900	\$261,298,900	
Copper (including that in alloys other than brass).....	112,400	130,600	113,350	113,350	144,100	193,200	196,500	250,600	281,700	
Scrap brass remelted.....	249,700	259,800	148,500	148,500	274,000	311,000	274,900	250,600	283,000	
Lead as metal.....	55,684	56,350	46,370	46,370	75,480	90,400	112,400	112,400	125,000	
Lead in alloys.....	66,416	68,300	57,410	57,410	84,080	98,000	113,486	113,486	152,300	
Zinc as metal.....	39,910	42,850	33,833	33,833	66,314	63,210	58,586	61,430	164,570	
Zinc in alloys other than brass ¹	6,062	7,650	5,340	5,340	10,250	9,689	7,700	13,300	13,430	
Tin as metal.....	5,977	7,200	5,400	5,400	6,570	5,282	7,700	7,950	9,750	
Tin in alloys and chemical compounds.....	18,056	16,300	11,500	11,500	12,910	22,315	23,600	23,600	23,650	
Antimony as metal.....	48	200	29	29	6,982	7,776	9,314	10,839	13,320	
Antimony in alloys.....	4,351	5,400	4,691	4,691	7,198	6,800	10,350	17,700	20,500	
Aluminum as metal.....	6,017	5,000	3,650	3,650	9,100	14,500	16,650	26,300	23,700	
Aluminum in alloys.....	12,674	10,500	5,286	5,286	104	177	165	191	485	
Nickel as metal.....	163	270	89	89	1,408	1,373	2,126	2,109	2,565	
Nickel in non-ferrous alloys and salts.....	2,584	1,950								
Total quantity.....	579,742	612,350	436,768	436,768	701,626	833,611	814,330	882,600	1,016,880	
Total value.....	\$181,811,500	\$188,507,260	\$89,140,500	\$89,140,500	\$143,891,700	\$205,418,600	\$200,578,600	\$243,570,700	\$274,540,900	

¹Secondary zinc does not include scrap and dross used for lithopone, oxide, zinc dust, or chloride. The use for some of these, especially for zinc chloride, is quite large.

SECONDARY COPPER RECOVERED IN 1925-26, WITH IMPORTS AND EXPORTS OF BRASS
AND COPPER SCRAP, IN SHORT TONS

	1925	1926
Copper as metal.....	183,700	200,100
Copper in alloys other than brass.....	66,900	81,600
	<u>250,600</u>	<u>281,700</u>
Copper from new scrap (not including brass).....	50,000	55,000
Copper from old scrap (not including brass).....	200,600	226,700
	<u>250,600</u>	<u>281,700</u>
Brass scrap remelted:		
New clean scrap.....	110,000	125,000
Old scrap.....	132,300	158,000
	<u>242,300</u>	<u>283,000</u>
Copper content of brass scrap:		
New clean scrap.....	79,200	87,500
Old scrap.....	90,410	110,600
	<u>169,610</u>	<u>198,100</u>
Total secondary copper (including copper content of brass scrap):		
From new scrap.....	129,200	142,500
From old scrap.....	291,010	337,300
	<u>420,210</u>	<u>479,800</u>
Brass scrap imported.....	5,374	4,311
Scrap copper imported.....	5,214	5,501
Brass ingots, scrap, and old exported.....	48,189	25,132
Scrap copper exported.....	6,053	9,713

The proportion of secondary copper recoveries compared with smelter production of copper from domestic ores for 1910-1926, was approximately:

	PER CENT.		PER CENT.
1910.....	18	1922.....	71
1915.....	28	1923.....	57
1918.....	37	1924.....	47
1919.....	44	1925.....	50
1920.....	51	1926.....	55
1921.....	86		

The quantity of secondary copper recovered in 1926 by plants refining primary metal was more than 112,000 short tons, which was about 35,000 tons more than such plants recovered in 1925. A large quantity of scrap copper and brass goes directly to foundries, and immense quantities of scrap are being exported to Europe. After the close of the World War, the imports from Europe were large, as Europe needed money more than old metal.

SECONDARY LEAD RECOVERED IN 1925-26, IN SHORT TONS

	1925	1926
Secondary lead recovered by smelters that treat mainly ore.....	35,146	32,499
Secondary lead recovered by smelters that treat only scrap and drosses.....	77,274	92,501
	112,420	125,000
Secondary lead recovered in remelted alloys:		
Lead content of antimonial lead scrap treated at regular lead smelters.....	9,483	11,554
Lead content of drosses and scrap alloys treated at secondary smelters.....	104,977	140,746
	114,460	152,300
Total secondary lead recovered.....	226,880	277,300

PRIMARY LEAD PRODUCED IN 1925-26, IN SHORT TONS

Refined primary lead produced in the United States:

From domestic ore.....	654,921	680,685
From foreign ore and base bullion.....	112,048	118,256
Lead content of antimonial lead from foreign and domestic ores and bullion treated at regular smelters.....	17,043	19,831

Proportion of secondary lead recovered to recovery of domestic refined lead:

	PER CENT.		PER CENT.
1910.....	14	1922.....	33
1915.....	15	1923.....	34
1918.....	17	1924.....	34
1919.....	24	1925.....	35
1920.....	25	1926.....	41
1921.....	25		

The increased percentage since 1922 has doubtless been due largely to the growing quantity of lead from old batteries.

SECONDARY ZINC RECOVERED AND PRODUCTS MADE FROM ZINC DROSS, SKIMMINGS, AND ASHES, IN 1925-26, IN SHORT TONS

	1925	1926
Secondary zinc recovered by redistillation.....	39,181	40,799
Secondary zinc recovered by sweating, remelting, etc.....	22,249	23,771
Total zinc recovered unalloyed.....	61,430	64,570
Zinc recovered in alloys other than brass.....	13,300	13,430
Zinc recovered in brass (estimated).....	53,300	63,000
Zinc dust made from zinc dross.....	5,813	4,889
Zinc dross used for zinc dust (estimated).....	6,850	5,732
Lithopone made from zinc skimmings and ashes.....	48,705	45,356
Secondary zinc content of lithopone.....	9,741	9,204
Zinc chloride made from zinc skimmings, ashes, etc.....	45,772	43,106
Zinc content of zinc chloride made from zinc skimmings, etc.....	10,070	9,481
Zinc content of zinc sulfate made from zinc skimmings, ashes, etc...	858	603
Zinc concentrates and ore exported.....	68,951	95,252
Zinc dross exported.....	15,968	10,461

Part of the zinc obtained by redistillation of zinc drosses and skimmings is recovered at smelters, which mainly use ore; the remainder is recovered at plants that treat zinc drosses in large graphite retorts. As shown above, large quantities of zinc dross, ashes and skimmings (averaging in recent years about 25,000 to 30,000 tons of zinc content) are utilized to make zinc dust, lithopone, zinc chloride and zinc sulfate, and considerable zinc dross is exported. Complete data for all years are not available, nor are such uses of zinc wastes accounted for in the large table attached; thus it is difficult to give the yearly proportion of zinc from secondary sources as compared with zinc derived from ore.

The proportion of zinc recovered as metal and in alloys, including brass, to the output of primary zinc of domestic origin is as follows:

	PER CENT.		PER CENT.
1915.....	19	1921.....	39
1916.....	16	1922.....	39
1917.....	17	1923.....	27
1918.....	23	1924.....	23
1919.....	23	1925.....	22
1920.....	25	1926.....	23

Only a very small proportion of the zinc coating on sheets and forms is recovered, and only a few thousand tons of galvanized scrap is treated.

In smelting brass there is considerable loss of the zinc content—a loss much greater than of the copper content.

SECONDARY TIN RECOVERED IN 1925-26

	1925	1926
Recovered as pig tin, short tons.....	7,950	9,750
Tin recovered in alloys and chemical compounds, short tons...	23,000	23,650
	30,950	33,400
Clean tin-plate scrap treated at detinning plants, long tons....	172,432	194,494
Old tin-coated containers treated, long tons.....	1,167	11,942
Metallic tin recovered at detinning plants, pounds.....	1,932,850	2,292,000
Tin content of tin tetrachloride, tin bichloride, tin oxide and tin crystals made at detinning plants, pounds.....	4,264,340	4,094,000
Total tin recovered at detinning plants, pounds.....	6,197,190	6,386,000
Tin tetrachloride, tin bichloride, tin oxide and tin crystals made at detinning plants, pounds.....	8,626,387	8,634,000
Average quantity of tin recovered per long ton of clean tin-plate scrap, pounds.....	35.8	32.7
Average quantity of tin recovered per long ton of old tin-coated containers, pounds.....	25	16.74

TIN AND TIN CONCENTRATES IMPORTED AND TIN PRODUCED FROM IMPORTED CONCENTRATES, IN 1925-26, IN SHORT TONS

	1925	1926
Tin imported as metal.....	85,843	86,418
Tin concentrates imported (tin content).....	214	339
Tin produced from foreign concentrates smelted in the United States		339

The largest recoveries of unalloyed tin are from tin scruff and drosses, and tin recovered in alloys is largely contained in solder, babbitt and bronze.

As only a few tons of domestic tin ore have been treated in recent years and tin derived from imported concentrates smelted in the United States is negligible in quantity, the secondary recoveries are best compared with the imports of primary tin. These imports were 85,843 tons in 1925 and 86,418 tons in 1926, and the secondary tin recovered amounted to 30,950 short tons in 1925 and 33,400 tons in 1926.

Probably 30,000 tons of tin are consumed in the United States by tin-plate makers. Scrap tin-plate clippings and waste are being treated at several plants in increasing quantities. Nearly 195,000 long tons were treated in 1926 and more than 3,190 short tons of tin mainly in compounds such as tin chloride, tin oxide, etc., were recovered from this scrap.

The large waste in tin is in used tin-coated containers, of which only about 12,000 tons were detinned in 1926, although existing plants have a capacity of more than 40,000 tons a year.

High costs of collection and shipping and the inferior grade of steel scrap recovered restrict the use of old tin-coated cans.

As tin is a relatively high-priced metal there is probably an adequate saving in scrap material other than old cans.

SECONDARY ANTIMONY RECOVERED IN 1925-26, IN SHORT TONS

	1925	1926
Secondary antimony in antimonial-lead scrap smelted at regular smelters.....	1,328	2,550
Secondary antimony recovered at secondary smelters.....	9,512	16,230
	10,840	18,780
Antimony imported in ore, as metal, or as oxide or salts.....	13,182	17,364
Primary antimonial lead produced at regular smelters.....	19,667	22,524
Antimony content of primary antimonial lead.....	2,624	2,693

Some antimonial lead is made in the United States directly from domestic ores, but the antimony from this source is less than 20 per cent. of the normal imports of antimony in ore or as metal. Since most of the antimony used goes into type metal, babbitt and batteries, which are easily collected, the secondary recoveries are large. In 1926, secondary antimony nearly equalled the antimony imported plus the antimony content of primary antimonial lead. The pigment, enamel and ceramic industries yield very little secondary antimony.

SECONDARY ALUMINUM RECOVERED IN 1925-26, IN SHORT TONS

	1925	1926
Secondary aluminum recovered unalloyed.....	17,700	20,500
Aluminum recovered in alloys (mainly No. 12).....	26,300	23,700
	44,000	44,200

PRIMARY ALUMINUM PRODUCED, IMPORTED, AND EXPORTED IN 1925-26

Value of primary aluminum produced in the United States	\$36,430,000	\$37,583,000
Aluminum (crude and semicrude) imported for consumption, pounds.....	41,997,178	71,391,717
Aluminum (crude and semicrude) exported, pounds.....	12,642,034	7,634,171

Mineral Resources reports do not give the quantity of aluminum production, though the value is given. Following is the percentage of recovery of scrap aluminum and aluminum in alloys, compared with the domestic output of aluminum given by the American Bureau of Metal Statistics:

	PER CENT.		PER CENT.
1913.....	15	1920.....	23
1914.....	12	1921.....	33
1915.....	27	1922.....	44
1916.....	42	1923.....	33
1917.....	26	1924.....	36
1918.....	26	1925.....	59
1919.....	29	1926*.....	

*About same as 1925, no production figures given.

The imports of aluminum are very large and the ratio of secondary material to virgin metal would be much lower if imported metal was added to domestic production.

In 1913 and 1914 the secondary aluminum recoveries reported probably were incomplete.

In 1925 the imports of aluminum were large, and those for 1926 were 15,000 tons more than in 1925.

Aluminum clippings and drosses are the chief source of recovered pig aluminum; defective castings, borings, dross and old castings supply the aluminum recovered in alloys. Since 1916 the amount of aluminum in alloys has been larger than that recovered unalloyed.

SECONDARY NICKEL RECOVERED IN 1925-26, IN SHORT TONS

	1925	1926
Nickel recovered as metal.....	191	485
Nickel recovered in non-ferrous alloys and salts.....	2,109	2,565
	2,300	3,050

PRIMARY NICKEL PRODUCED, IMPORTED AND EXPORTED IN 1925-26, IN SHORT TONS

Nickel produced as a by-product from the electrolytic refining of copper at domestic refineries.....	272	306
Nickel imported for consumption in the United States as nickel, or in ores, matte, oxide and alloys.....	21,536	22,765
Nickel, monel metal and other alloys exported.....	1,285	799

No production of primary nickel has been reported from domestic mines for several years. The only primary nickel—and that not necessarily of domestic origin—is a by-product from the electrolytic refining of

copper. No inquiry has ever been made concerning the quantity of nickel contained in remelted ferrous alloys, although that is probably still the largest source of secondary nickel.

The recoveries from non-ferrous alloys have increased rapidly and will increase further as the uses of non-ferrous nickel alloys in peace-time manufactures continue to increase.

The total value of the secondary metals included in the inquiry during the period 1910-1926 has been about \$2,773,000,000, about \$726,000,000 more than the combined value of the gold and silver production in the same period.

With industrial expansion and greater consumption of primary metals the recoveries of waste will increase, for large companies with adequate equipment and with widely distributed plants and agencies now handle the bulk of metal wastes. Buying in large quantities and employing chemists and metallurgists, they use materials to the best advantage and sell metals and alloys on close specification or by brands.

Business ethics of the trade have improved, and rigorous competition has caused expansion in the size of plants and in the reliability of their products, so that there are few users of metals who can afford to ignore the saving possible by the use of some reclaimed material.

DISCUSSION

W. C. HIRSCH, Rahway, N. J. (written discussion).—The author presents the interesting information that ours is the only one among the world's governments to distribute data pertaining to waste metals and drosses. To this may be due, in no small measure, the contrast presented by conditions in the secondary metals industry here and abroad. Only the other day, I read in a London trade publication an article in which the writer, after singing the praises of statistical information available regarding virgin metals, said: "To this laudable state of affairs scrap forms an exception, for it furnishes no record of business done, scorns 'official' prices, conforms to no standard of form or purity, and leaves the estimation of quantities available, and likely to accrue, to those sufficiently interested in old metals to gather such meager information as can be got from a study of 'disposal sales.'"

The self-discipline which the American trade has imposed upon itself through the National Association of Waste Material Dealers has been made possible to a large degree by the moral support and sympathetic attitude of the U. S. Geological Survey and later of the U. S. Bureau of Mines, so that, aside from the valuable statistical service rendered by the author of the paper under discussion, he and his mentor, C. E. Siebenthal, have done much to overcome the prejudice that used to take the form of the question: "Can any good thing come out of the junk business?"

Moreover, they have stimulated thought along constructive lines with reference to the economic status of secondary metals, in proof of which it is but necessary to cite a recent study from the pen of A. B. Parsons,¹ presenting an admirably comprehensive and profoundly sound analysis of the influence of scrap supplies on the markets for virgin metals.

¹ A. B. Parsons: How and Why Salvaged Scrap Affects Markets for Virgin Metals. *Eng. & Min. Jnl.* (1928) 125, 286.

Dunlop notes the much more efficient handling of scrap at its source and marked progress in its treatment in the plants of secondary smelters, due to the employment of competent metallurgists. The war made American industry scrap-conscious in more sense than one. While we were still in it, and did not know how long it might continue, I wrote a series of articles on Warring on Waste,² which were published in an industrial, monthly magazine, and which, in part, Dunlop had the kindness to embody in his annual report. I concluded this series of articles thus:

"Properly managed the equipment provided for the conservation of scrap and the time and effort expended in its systematic accumulation, supervision, and disposal will prove not only directly profitable, but the indirect return which will come from the enhanced care that will be accorded to new material is certain to prove of incalculable value. There is perhaps no more reliable index to the state of an industrial enterprise than the manner in which its scrap is handled. The day of the salvage expert is beginning to dawn. At first he will have to work out his own salvation. Later his vocation will become a profession, the theory of which will be taught in universities and colleges. American industry will be decidedly the gainer when the industrial salvage expert has come to be commonplace and indispensable in the average plant."

This and kindred propaganda from more influential sources has borne and continues to bear fruit. Large industrial scrap producers, frequently also large consumers, are keenly alive to the vital importance of the subject, and, if the smaller manufacturer wants to stay in the ring, he must follow suit.

But while, as Dunlop intimates, industry has made marked progress along the line of scrap conservation and utilization, household, farm, garage and the small workshop have hardly kept pace with this advance. Travel along the highways and byways of the country, and you can not help seeing abandoned wrecks of motor cars lying by the wayside or in shoals in wreckers' yards, brass and aluminum rusting away. In 1919, the Waste-Reclamation Service of the Department of Commerce issued a brochure with this slogan: "Don't Waste Waste—Save It." It was written for the mass of the American people, and contained such facts as the following:

100 lb. of scrap zinc will make about 75 lb. of new zinc.

100 lb. of scrap lead will make about 93 lb. of new lead.

100 lb. of aluminum castings converted into ingots will make 94 lb. of new aluminum.

Sheet-aluminum scrap shrinks about 10 per cent. and aluminum turnings from 15 to 25 per cent., while new clippings or cuttings shrink from 1.5 to 3 per cent.

100 lb. of heavy scrap copper will make 95 lb. of new copper.

100 lb. of light copper will make 90 lb. of new copper.

Just as the increased cost of distribution of the necessities of life has become a burning problem, so the increased cost of collecting household, motor and miscellaneous scrap should be brought into the foreground of discussion. Low prices for virgin metals threaten to completely dry up this important source of scrap supply, and when a national emergency arises we shall be the sufferers. Poke all the fun you want at the junkman, but keep him in business. After all, economically, he takes his place by the side of the miner, and look at all the praises that poets have heaped upon that noble calling.

The scrap-metal merchant really deals with two distinct classes of scrap. One consists of unalloyed scrap, such as crucible copper, tea-lead, block-tin pipe, zinc and aluminum clippings. I have yet to hear a convincing argument why these should be quoted on any other than a percentage basis of their respective primary metals, allowing for melting loss and cost. In practice, of course, their price is made on that very basis, but the unfortunate part is that separate quotations, expressed in cents instead of per cent. of virgin-metal prices, tend to create in the minds of many consumers the

² *Factory* (1918) 20, 494, 740.

erroneous impression that a wide gulf separates scrap from virgin metals, when, in fact, crucible copper scrap, metallurgically, is on a parity with casting copper quoted in the list of primary metals, and frequently a secondary product. When the question of fixing maximum prices for certain scrap metals came before the War Industries Board, Pope Yeatman, chief of the Non-ferrous Metals Division, took the very logical attitude that scrap copper was, in fact, copper, and that, therefore, the maximum price established for the virgin metal applied *per se* to its *alter ego*.

The other class of scrap with which the merchant deals consists of alloys and drosses. Their value is determined far more by the ingenuity of the specialist who treats them and leads them into that avenue of consumption where they can be most economically utilized than by mere market conditions.

Study of the figures presented by Dunlop covering the proportion of secondary copper recoveries compared with smelter production of copper from domestic ores drives home the thought whether it is not high time to preach the idea that, barring the exceptions that prove the rule, it is a crime to use virgin copper for casting, even when the primary market is extremely low. Virgin metal is indispensable in wire-drawing, where high conductivity, aside from purity, is essential, and in rolling some products, especially for electrical use. Is it not economically wrong to use it where secondary metal will give as good satisfaction, and save heat besides?

Dunlop makes mention of the heavy exports of scrap now finding their way to Europe. Others have had the same thought as I on this subject, that resistance to the American copper export combine was directly responsible for Europe's appetite for American cuprous scrap. In this, scrap is simply performing its historically traditional function as a market corrective. The Secretan Syndicate, which set out to corner the world's copper supply in 1887, went to smash in 1899 because thousands and thousands of tons of scrap copper were thrown on the market. Scrap copper also had its share in defeating the attempt of Amalgamated Copper Co. to corner the supply.

The peace-time importance of secondary metals, our second line of defense in time of war, is steadily growing. Scrap holds the balance of power in the metal markets, preventing combinations of producers from overreaching themselves. More light is needed on our invisible supplies, and the rapidity or perhaps slowness with which metals in their various uses return as scrap. Certain it is that there will be a steadily widening field for the technical knowledge and systematic research of the metallurgist who, grounded in the metallurgy of all commercial metals, makes the efficient and economic utilization of secondary metals as much his life's work as has J. P. Dunlop their statistical study.

J. P. DUNLOP (written discussion).—I quite agree with Mr. Hirsch. The day of the salvage expert is here. The "savers" will become nearly as important as the buyers and salesmen. Mr. Hirsch's suggestion as to quotations of scrap in percentage values is a good one.

Sampling and Evaluating Secondary Non-ferrous Metals

By T. A. WRIGHT,* NEW YORK, N. Y.

(New York Meeting, February, 1928)

THE SAMPLING of waste materials containing copper, lead and tin has taken on a new significance within recent years, and is of increasing importance, on account of the entry of some of the copper refineries into this field and the tendency towards consolidations among the smelters. In the past, such material was sold on the basis either of a rough or grab sample or of casual inspection of the lot.

The two principal sources of this waste are the processes of fabrication and the scrapping of automobile, electrical, plumbing, railroad and other equipment. In both cases much material can be sorted, salvaged and sold by classification and grade to be melted "as is" or with the addition of new or virgin metal. The increasing care in classifying exercised in the large manufacturing plants tends to increase the proportion of this usable scrap; on the contrary, the increasing use of more complex and special non-ferrous alloys tends to make sorting and grading more difficult in turnings, borings, clippings, etc., and consequently is making sampling of more moment.

In tin, lead, aluminum, and zinc furnace by-products such as ashes, drosses, skimmings, etc., the trade practice of evaluation has not varied much. For instance, tin drosses, battery lead, and aluminum skimmings are ordinarily sold on what is called "metallic button" or "metallic recovery" or "metallic yield." Copper and lead waste, however, is being sold more and more on actual copper and lead contents based on sample and chemical analyses.

This paper will be devoted chiefly to the sampling of materials suitable only for refining and recovery of one or more of the metals present. The methods described are often based on the fact that but one metal, such as copper, is to be paid for. The loss of volatile constituents in melting does not appreciably affect the final copper result, as the "after-melting" assay can be readily calculated to the "before-melting" basis, but if smelter efficiency continues to increase, so that in time zinc, for instance, may be recovered on a paying basis, the method of sampling dirty brass, for example, will have to be changed also.

As a matter of fact, we may expect that improved refining processes will make possible the partial recovery of lead and tin which are now lost.

* Secretary, Lucius Pitkin, Inc.

GENERAL PRINCIPLES OF SAMPLING SCRAP

Mathematics enters very little into the sampling of metallic scrap as such. The drawing of the sample is all important, and no substitute for personal selection made jointly by the representatives of the buyer and seller has yet been found. On the other hand, on copper-bearing material, as it is known in the trade, a definite ratio of the lot may be set aside and true coning, mixing and quartering practiced as in ore sampling. Table 1 shows a rather rough group of types in which selection has the larger importance and Table 2 those of which definite proportions should be taken. A combination method is advisable when judgment is a large factor and conditions admit: for example, in shipments of skimmings, there may be large chunks of metal; if the sample is being drawn by the tenth or fifth shovel or by an automatic mill the large metallics should be set aside, broken up with a sledge, mixed, quartered down and weighed. The final sample for melting should be made up of the proper proportions of fines and the broken metallics.

TABLE 1.—*Rough Grouping of Metallic Scrap When Selection is of Greatest Importance (Class A)*

Scrap Metal	Copper				Free Iron	
	*Sample	Per Cent.		May Contain	Per Cent.	
		High	Low		High	Low
Armatures.....	M-T	25	10		80	5
Arc lamps.....	M	66	27		50	0
Brass scrap.....	M	85	10		80	10
Breakage.....	M	65	30		35	0
Briquetted metal.....	M	99	45			
Bronze scrap.....	M	90	75	Sn		
Carburetors.....	M	83	73			
Coils—electric.....	M-T	90	17		66	0
Composition scrap.....	M	85	60	Sn		
Copper scrap.....	M	99	87			
Fields.....	M-T	50	25		70	20
Bottoms, furnace.....	M-D	93				
Generators.....	M-T	20	10		80	5
Gaskets.....	M	71	48		15	0
Radiators.....		Flat Rate		Sn-Pb	20	
Tuyeres.....	D	96	88			
Valves.....	D-M	88	45	Sn-Pb	5	
Wire and cable.....	M	31	13	Pb-Sn		
Copper-clad steel wire and BX	T	70	10		90	30
Tinsel, cordage, magnet wire...	M	50	20			
Insulated wire.....	M	91	30			

* M = Melt; T = Matte; D = Drill

TABLE 2.—*Rough Grouping of Metallic Scrap of Which Definite Proportions Should Be Taken (Class B)*

Copper and Lead-bearing Scrap	*Sample	Copper			Free Iron	
		Per Cent.		May Contain	Per Cent.	
		High	Low		High	Low
Ashes, all kinds.....	M-S	75	5	Pb		
Battery-plates.....	M	85	68	Pb-Sb		
Borings, all kinds.....	S-M	97	10	Sn	50	
Bronze powder.....	S	85	75	Sn		
Buffings, all kinds.....	S-M	65	9			
Carbon blocks and dust.....	M-S	79	69	Pb-Sn		
Cement copper.....	S	60	20		5	
Cobbings.....	M-S	25	15			
Concentrates, brass.....	M-S	70	5		10	
Copper cinders and clinkers....	S-M	30	7			
Copper oxide and scale.....	S	95	45			
Copper ingots and pigs.....	D-M	99	85	Sn		
Drosses (Cu, Pb, Sn, terne, solder, babbitt and die-casting).....	M-S			Sn-Pb	20	
Dusts, copper.....	S	85	15			
Fuses.....	M	60	30			
Filings.....	S-M	75	65		40	
Grindings.....	S-M	75	10		20	
Jack-strips.....	M	45	10		50	40
Lamp-bases.....	M	30	5			
Lead oxide and mud.....	S	70 Pb	45 Pb	Pb		
Lead sulfate.....	S	65 Pb	35 Pb	Pb		
Mattes.....	S	60	20			
Mud, foundry, rumbling.....	S	25	3			
Residues.....	S	40	25			
Shells, shotgun, brass, copper..	M	70	25			
Shells, electrotype.....	M	50	30	Pb		
Screenings, siftings, sievings...	S	70	45			
Skimmings (aluminum, brass, zinc sal-ammoniac).....	M	73	7	Pb-Sn-Zn-Al		
Slags, all kinds.....	M-S	21	0	Sb-Pb-Sn		
Spatters.....	M	65	35			
Sweats.....	M			Sn-Pb-Sb		
Sweepings.....	S-M	65	25			
Tailings, separator, magnet...	S	56	7			
Turnings, all kinds.....	M-S	99	23	Sn		
Washings.....	S	85	4			

* M = Melt; T = Matte; D = Drill; S = Screen

The aim at all times should be to minimize the personal equation, but to keep in mind that free metal is invariably present and that the lot is probably very unhomogeneous, or rather, heterogeneous.

In Class A (Table 1) the representatives of both buyer and seller select a number of pieces, which will be as nearly typical as is consistent with the weight and value of the lot. Hand work is not only unavoidable, but desirable. For example, a carload of briquetted or bundled wire may have "bricks" or "bundles" consisting wholly or in part of heavy insulated and cotton-covered wire, soldered ends of clean wire, lead-covered cable, and copper gaskets. Haphazard selection is wrong and taking every tenth may be very unfair; a number of each type, dependent on occurrence, should be taken and one-half of each "brick" sheared off and cut up into small pieces. The pile can then be mixed with shovels and quartered down to a weight of 10,000 to 30,000 gm. (20 to 60 lb.) and melted.

Another example would be armatures, which run, of course, very high in iron. A sufficient number of each type, which may be one of each or more, may be first stripped by hand. A greater net weight can then be melted unhampered by unwieldy amounts of iron.

In tuyeres, one or two should be selected and the inside scraped and cleaned before drilling, if possible. Obviously, the tuyeres taken for a sample should be weighed before and after cleaning, although no melting is done.

It should be evident from the cases mentioned that the sample taken may be anything from 1 to 50 per cent. of the lot of scrap.

In Class B (Table 2), however, a more or less definite scheme can be outlined to cover a sample of 1, 5, 10 or 20 per cent., depending on the percentage of free metallics and the particle size. The main point lies in the manner of taking the sample. Each man engaged in unloading the car should be assigned to a certain area and the removal of the material should be along a definite line, say from right to left or vice-versa, setting aside the fifth or tenth shovelful for the sample. Large metallics should be picked out by hand, broken down, weighed and added in the proper ratio to the main portion. Certainly the men unloading should not be permitted to shovel here or there, taking a sample shovelful whenever or even wherever they may choose. The only justification for a percentage sample is in the regularity of taking it. A carefully taken grab sample is better than every fifth shovel taken haphazardly.

In all cases, half the final crude sample should be held as a reserve in case of dispute.

MOISTURE DETERMINATION

In general, the regular sample will suffice. If the material is sold with payment to be made on the original or "as received" basis, it is necessary to ascertain the moisture, if for no other reason than the proba-

bility that the reserve portion may either lose or gain moisture in storage, and, of course, it is always advisable to dry before charging into a crucible. If the sample is to be screened only, either the sample must be dried at 212° F. and the resultant assay run on the "dry basis" or else the sample may be burned with or without the addition of kerosene oil. In either case it may be calculated to the "original basis."

If material is sold with payment and treatment charges on a dry basis, a moisture test must be run. The usual practice is to take either the regular sample or a portion (weighing, say, 10,000 gm.) and dry either in an oven or by the furnace. The moisture determination, therefore, may be very important, for it may not only reduce the treatment charges through smaller weights but may throw the material into a higher schedule and consequent lower rate.

The moisture determination, in most cases, should be made by drying at a temperature about 212° F. Fine material is sometimes calcined, but while this shows a loss of other volatile and combustible matter as well as moisture, this loss may be partly offset by oxidation of finely divided metal. As a matter of fact, material like copper cements and some mattes will show first a loss, but finally a gain when dried at slightly over 212° F.

Copper oxide or mud from wire or cable may contain both water and oil or grease. The samples are generally first dried and then burnt. Such moisture determinations are often unsatisfactory.

ELIMINATING OIL AND GREASE

In the sale of turnings, etc., for remelting purposes, the matter of oil and grease is often an issue. A 5 or 10 per cent. sample is taken of thoroughly mixed material, coned, quartered and remixed and placed in a container, preferably a bottle. When sold to a smelter, this class usually calls for burning the sample. Before and after burning weights must be taken. When sold to a brass foundry the turnings should be washed, first with alcohol and then with ether, before analysis, the loss in weight being ascertained.

REMOVING IRON

Whenever possible, free iron should be removed with a magnet or by hand before melting. If the sample is one that admits of screening, it is best to pick out by hand the larger pieces and use the magnet only on the coarse scales or metallies. If used on the fines, values may be removed at the same time, especially if oily. If the iron is attached to the other metals, as in armatures, generators, bed-rods and the like, it is sometimes possible to sweat the material. When necessary to actually melt the other metals, the iron should be taken out by skimming; it should always be weighed and the weight included in the sampling data

given on the bag. Unless carelessly done, the "wash" or copper adhering to such iron can be disregarded. If the material cannot well be sweated or melted into a good bar, the whole sample should be melted with the addition of sufficient sulfur to form a clean low-grade matte. This is especially advisable on material containing more iron than copper and in copper-clad steel.

SIZE OF THE SAMPLE

The weight of the final sample is dependent on (1) the melting equipment available and (2) the size and character of the pieces in the shipment. Ore can always be broken down and crushed; scrap rarely. The larger the particle size, the fewer the particles, and consequently the larger the sample required. The more varying the character of the pieces, the larger the sample required; 100 lb. might be none too much to melt of an iron composition, while 20 lb. might be plenty for dirty grindings or No. 2 wire.

For convenience, it has been the habit at some smelters to take even and definite weights for melting, such as 50 or 100 lb. (10,000 to 20,000 gm.). This is not good practice, for to get an even weight, something must be taken from or added to the final sample. Either a definite quarter or two quarters should be weighed "as is," whether selected by the shovel or by hand. There is no doubt that taking round figures, such as multiples of 10 or 100, minimizes clerical errors, in one way, especially in calculating the final assay, but the weights of the various portions after melting or screening are rarely even, so the clerical and mathematical advantages claimed are at least open to question.

MELTING EQUIPMENT AND PRACTICE

Copper, brass, scrap and copper-bearing material are usually melted in graphite crucibles, sizes from No. 100 to 150 being in general use. On account of the bulky nature of some of the scrap, it is best to be generous as to capacity. It is sometimes necessary to charge in several batches and possibly add more flux.

The furnaces may be either of the pit or tilting type, and are usually oil-fired. (Fig. 1 shows furnaces used by United States Metals Ref. Co. at Chrome, N. J.) One man can handle two furnaces, but two men are required for melts much over 50 lb. This increases sampling costs, which are, of course, passed on to the shipper, and increased accuracy gained by melting a larger sample may be more than offset by the increased sampling charges.

All the samples should be delivered to the melter in containers plainly marked with the lot number. The charge can be placed in the crucible and the necessary flux added. Borax is generally used alone or with additions of charcoal, soda ash, and sometimes sand, depending on the material. Salt should not be used with samples in which the copper and

tin are to be determined, and in melting all samples for lead, tin and antimony, care must be taken to avoid excessive heat in melting.

A crucible will give 12 to 14 melts, on the average. Clean copper-bearing material will give from 18 to 20 melts; very dirty and irony material from 5 to 10, and battery lead rarely over 7 or 8 melts. High-zinc and irony samples are the hardest on crucibles.

After the sample is properly melted the free iron may be skimmed off into a pan; tagged, cooled and weighed. The slag is then skimmed into a pan, or better still, poured with the metal into a mold, the slag broken loose and weighed. If very small in amount or of a light color, it can be disregarded altogether. This is usually the case in heavy and light



FIG. 1.—FURNACES USED BY THE UNITED STATES METALS REFINING CO., CHROME, N. J., FOR MELTING SAMPLES OF COPPER-BEARING MATERIAL.

copper, clean brass, etc. Slags from furnace products, dirty scrap, etc., should be weighed, crushed to 60-mesh and sieved.

Shot will often be found. Experience has shown that the copper assay of this shot will rarely vary more than 3 per cent. from copper assay of the bar, so that it is generally cheaper and sufficiently accurate to weigh the shot, deduct the weight from the slag and add the weight to the bar, thus saving an assay. The slag as ground is mixed, quartered and bagged. If it is necessary to remelt a bar because of hard irony shots, it is best to add more flux. The weight of the second slag should be added to that of the first, and the two should be mixed.

After skimming, the melt is poured into a flat slab or bar, preferably not over 1 in. thick. Drillings should be taken from all portions, drilling through each time. The drillings should be mixed carefully before bagging, but it is rarely necessary to grind them.

Great care must be taken in tagging and marking, and the stamping of the bar is especially important, for it is the heart of the sample.

The after-melting, or A. M., weight should be taken and noted; in fact, all weights pertaining to any sample should be checked by two men. This point cannot be stressed too much.

PREPARATION OF SAMPLES

After the sample has been selected by one or the other of the methods described, it may be prepared by one of several different schemes, depending on a number of conditions, governed (1) by the facilities at hand; (2) by the weight and approximate value of the lot; (3) by the size and character of the material. The methods at this stage of final preparation comprise melting, screening, and matting.

Melted Samples

Melting is the method generally used. The material, either dried or undried, may be charged directly into a graphite crucible or the fines may be screened out and only the coarse material melted, with or without prior removal of the iron.

Screened Samples

Material suitable for screening is usually dried first, for obvious reasons. It may also need grinding or crushing in a mill or possibly by a jaw-crusher and set of rolls. Sieves 30 to 60 mesh are used, dividing the samples into portions called fines and metallics, or pulp and scales.

It is generally advisable to assay each portion separately. The iron in the scales, shot or metallics should usually be removed with a magnet. No attempt should be made, however, to remove iron in this way from the fines or pulp portion.

It may be good practice to melt the coarse portion if it is sufficiently large and unhomogeneous. Before and after melting, weights should be taken. In melting, it may be advisable to add a small amount of borax, but it rarely is necessary to weigh or analyze the small amount of such slag.

Matted Samples

For iron material, this method, when it can be conveniently used, is best of all from the standpoint of accuracy. When properly carried out the resultant matte can be crushed, pulverized and thoroughly mixed. Only one determination of copper is necessary and the buyer's and seller's assays should and do check within 0.25 per cent. or less. It is peculiarly suited for iron material but the cost is high and very few smelters have facilities for getting a high enough heat, so that often a slag will contain free metal. This slag must be ground and separated into fines and shot, making three portions of the sample to be assayed.

The final result, though more nearly correct, may have increased the sampling costs beyond reason.

On the other hand, some samples have so much iron not readily removed except by melting that, despite the care used in skimming after sweating, the resultant bar contains hard spots, which easily break a drill. Such a bar must be remelted with additional flux, thus giving two slag weights and two A. M. weights for the bar, with a consequent increase in labor and fuel cost and still further chance for clerical errors and losses.

ALUMINUM SCRAP, DROSSES AND SKIMS

Aluminum scrap is rarely sold on joint sampling at the works of the buyer. One of the largest works handling this confines its purchases chiefly to material of which the origin and composition are known.

Drosses and skims, however, require some form of sampling, as they are sold on the basis of "metallic or free aluminum," no payment being made for the oxide. Up to recent times the practice has been to draw a sample by either the grab or shovel method, reduce in quantity, crush somewhat if necessary, and screen through a 60-mesh sieve, discarding the fines obtained and fluxing only the coarse.

The free metal having settled to the bottom of the crucible, the heat is continued a few moments and the crucible removed, cooled and broken. After cleaning, the button may be sawed for purposes of analysis. As a rule, only the aluminum is paid for, but the button may contain other metals present in the original alloys; copper, for instance.

Tests made in our laboratory with zinc chloride and calcium fluoride, the usual fluxes given out in the trade, indicated that the finely divided metal contained in the portion under 60-mesh was not recoverable. We have reason to believe that a change in the method of fluxing would partly avoid oxidation of particles as fine as 80 mesh.

BRASS AND COPPER SKIMMINGS

This material will usually contain metallics of appreciable size. It may be sampled by hand by the tenth shovel, or "one and nine," as it is sometimes called, or it may be passed through an ore-sampling mill. The latter is a distinct innovation in sampling practice, introduced at the copper refinery of the United States Metals Refining Co. at Chrome, N. J. The mill is used only for carload lots.

As in hand sampling, large metallics should be picked out and broken with a sledge. If there are many of these, they should be weighed and a proportionate amount added to the main sample as delivered from the last cutout used in the mill; if few, they may be broken up and thrown in with the rest of the material. The mill is equipped with four cutouts (any one or all can be used), each giving a 20 per cent. cut. If the particles are of sufficient size, the material may be passed through a jaw-

crusher, gyratory crusher and three sets of rolls in the order given. The full use of the cutouts will give a sample equivalent to $\frac{1}{625}$ of the lot with a weight ranging from 150 to 250 lb. Depending on the setting of the final rolls, the maximum particle size will vary from 0.25 to 1 in. This sample may then be passed through a laboratory-size crusher, quartered once or twice as needed and melted to a bar and slag.

Ashes, cinders, clinkers, cobbing, concentrates, drosses, muds, residues, slags, fine spatters, sweepings, tailings and washings are sampled in a like manner except that they need no crushing, as they contain only fine material. They should be screened and assayed "as received" and not melted.

LEAD DROSSES AND SKIMMINGS

Waste of this type may be sold on the "metallic button" or total lead content basis. In either case, after a sample is obtained by the shovel method, it is melted down under a reducing flux.

If the contract calls for "metallic," most of the lead, tin and antimony will be in the button, together with some of the impurities such as copper, arsenic, etc. If "total lead" is called for, both the button and slag are assayed and the flux used is of a more simple nature, no care being taken in reducing other than to get a clean slag, which may contain as high as 60 per cent. lead. In the "metallic" melt, the flux is highly reducing, the losses of metal retained in the slag being *partly* compensated for by the somewhat impure button thus obtained.

BATTERY LEAD OR PLATES

This consists of old wet batteries of the automobile and radio type, and the lead plus antimony will vary from 70 to 85 per cent. The antimony will run from 3 to 4 per cent. as a rule. The container is usually not shipped and there is a marked tendency to cut off the lugs and sell separately. There is always more or less dirt but in the past most of the trouble has been from the moisture. Some have dried at 100° C. (212° F.) but the better practice today is to bake the sample.

On an average, the shipment will consist of lugs, connectors, plates, oxide and sulfate from the plates, and wooden or rubber separators. The separators will make up from 7 to 10 per cent. of the wet mass and will show a moisture about 10 times as high as the plates and lugs combined. The lugs will assay about 96 to 98 per cent. lead and antimony. An average lot of battery plates should contain around 8 per cent. lugs; a lot may have none; if mostly whole batteries, it might show as high as 15 per cent.

The plates and oxide, then, make up the bulk of the material and the difficulty in sampling is to get a proper ratio of plates, lugs and separators; or liners, as the last are sometimes called. The proper procedure is to

take every fifth or tenth shovel, as the case may be, and when the sample is drawn have it weighed. Break and cut off the lugs and weigh to find out the percentage of lugs in the material. Break up and crush the plates and liners, mix and quarter down to approximately 100 lb. Then combine the proper proportions of lugs and plates for the melt sample. Of course, a reserve sample should be held and moisture run at a temperature high enough to drive off moisture and other volatile matter but not high enough to melt or sinter the sample.

The smaller the sample melted the more care must be taken, although if brought to a fine state of division a portion as low as 100 gm. may be melted in a clay crucible; the latter cooled and the button broken out and weighed. This practice is followed at the works of one of the large smelters and is probably the cheapest in labor, fuel and material.

Another works, which buys on metallic yield, melts from 250 to 350 lb. in a large kettle. The slag must be skimmed off and the metal ladled out into bars. The cost is high and the time long.

Trade practice in general calls for "metallic yield," "metallic button," "metallic recovery" or "metallic" (all four terms being synonymous) as the final operation of determining the value of battery lead and similar material; and there is little doubt that when properly carried out the results may be sufficiently near the truth. As mentioned before, the button is weighed and is assumed to be Pb + Sb. The slag is assumed to contain no more Pb + Sb than will be lost by the smelter in refining and is, therefore, disregarded in this method. Ordinarily then, there will be no necessity for analyzing the button or the slag. As a matter of knowledge, a 300-lb. sample, typical of the practice at one works purchasing on the metallic basis, was thus melted and assayed. The metallic, or button, was 78.10 per cent.; the slag amounted to 6.78 per cent. of the sample. The partial analyses of each and the calculations showing the comparative and composite values is given in Table 3.

Our experience is that on a large melt, the sample is more representative but the metallic yield is too low because of the character and amount of slag. Conversely, on a small melt, it is more difficult to obtain proper proportions of lugs, plates, liners and oxide but the slag is more apt to be relatively small and clean.

In another experiment in our laboratories, the total of the actual Pb + Sb was 0.50 per cent. more than the metallic button run down on a large portion of the same sample.

Pb + Sb = 83.00 per cent. vs. metallic button, 82.50 per cent.

The slag on the first sample was high in both lead and antimony. The slag on the second, as usual, was not saved and analyzed.

The better practice, therefore, in the opinion of our organization, is to melt from 50 to 100 lb. in a large crucible to a clean slag free from shot.

TABLE 3.—*Partial Analysis of Typical 300-lb. Sample*

	Lead, Per Cent.	Antimony, Per Cent.	Tin, Per Cent.	Arsenic, Per Cent.	Copper, Per Cent.	Iron, Per Cent.
Analysis						
Bar.....	94.54	4.85	0.23	0.10	0.00	0.27
Slag.....	39.57	2.93	1.01	1.33	1.75	4.28
Reconciliation						
Bar (78.10 per cent.)..	73.83	3.79	0.18	0.08	0.00	0.21
Slag (6.78 per cent.)...	2.68	0.20	0.07	0.09	0.12	0.29
Sample.....	76.51	3.99	0.25	0.17	0.12	0.50
						PER CENT.
Metallic yield — lead + antimony + impurities.....						78.10
Lead plus antimony as assayed.....						80.50
Difference.....						2.40

The slag is skimmed and crushed. Either the melt is poured, the slag broken off and the bars sawed, or a dip sample of the metal is taken and poured into a small bar, which may be rasped down. The weights of both metal and slag are taken and both portions assayed for lead and antimony, payment being made on that basis, less the usual deduction and with a premium or penalty for plus or minus 80 per cent. lead plus antimony.

Baking losses will run as high as 15 per cent., called "moisture," but most contracts specify or allow 1 per cent. The average is 5 to 7 per cent.

TIN AND TERNE DROSSES, SKIMS AND ASHES

Tin drosses are often sold on the basis of "metallic button" or "recovery." They may contain as high as 35 per cent. moisture and much zinc and ammonium chlorides. In this wet condition they are in the form of a thick sludge and the sample is best taken while barrels are being loaded. A sample of 10 per cent. or 5 per cent. should be sufficient. (Another method of drawing is to pour off the water, mix and take a pipe sample of the sludge.) After mixing thoroughly the sample is placed in two-quart glass jars, covered tightly, and both barrels and sample are weighed. The sample is then sent to the laboratory and washed thoroughly by decantation, dried and weighed. It may be then passed through a set of laboratory rolls, sieved through a 40-mesh sieve and the metallics or scales weighed. The pulp or fines is best taken by difference. If sold on "metallic button" by the "coal" method, disagreements are minimized by making a joint assay in the presence of both buyer's and seller's representatives.

Coal Method

Proportionate amounts of fines and scales, together with a flux made up of soda and hard-coal dust, are mixed in a small crucible. Four times as much flux as sample is taken and the latter may be from 100 to as much as 400 gm. Triplicates are made up and melted in a gas, coke or oil furnace. The melt, when not cooled in the crucible, is preferably poured into a flat bar rather than a button. If it is to be analyzed, raspings are better than sawings. Segregation in bars, from drosses containing antimony and lead, is marked, so the raspings should be thoroughly mixed. As a matter of fact, at least two melts should be taken and averaged. The slag is ignored. Results are low but are claimed to be in line with smelter recovery. As much as 4 to 15 per cent. of tin may be lost.

Cyanide Fusion

The cyanide fusion is less often used to ascertain the metallic button and is carried out in a manner similar to the old determination in tin ores, using twice as much cyanide as sample. It is not suitable forterne drosses. A more accurate method is to screen the sample through a 40-mesh screen after reducing. A cyanide fusion on 10 gm. in triplicate will give a button on the fines, which may then be rasped down.

If much iron is present the button will have hard spots and care must be taken again to avoid segregation. The coarse screenings will be of a scaly character and usually brittle. They may be further cut and broken down, riffled or melted under a flux or with resin, cast into a bar, weighed and rasped or sawed. Correction must then be made for the melting loss.

Iron is an impurity and may be penalized. If present in sufficient quantity the determination can be made only by a wet method on the original material. Lead is also best assayed in a similar way.

Most Accurate Method

The most accurate method of all for such material is the one employed at the Balbach Works of the United States Metals Refining Co. on solder drosses, sweated radiator dross. This consists of melting 20 to 60 lb. of a suitably prepared sample with soda and charcoal, in a graphite crucible or large ladle. The slag is crushed and ground and the bar may be sawed lengthwise and one-half rasped down. Both bar and slag are assayed.

ZINC ASHES, DROSSES AND SKIMMINGS

These may be very wet and full of salts such as zinc and ammonium chloride or they may be dry with practically no chloride. They are sold on "sample," the latter being often but a grab wrapped in paper, whether

wet or dry. Determination is always required for the total zinc content and often for the moisture and chlorine, the latter being penalized. In sampling, care should be taken to obtain the proper proportion of metallics and fines. The sample is best bottled.

LAMP BASES

This material consists of the scrap from electric-light bulbs. The glass from the bulb itself is usually present in only a small amount, but that from the inner tube in which the wires are sealed will be present in varying amounts in the shipment. A base will consist of four parts, the ratio by weight of each part being as follows:

	STANDARD TYPE 1 IN. DIAM. PER CENT. BY WEIGHT	LARGE TUBE 1½ IN. DIAM.
Brass shell.....	20	25
Wax or plaster.....	49	37
Glass tube.....	30	37
Lead-in wires.....	1	1

The material is sometimes shipped "as is." The copper content will vary from 5 to 30 per cent., although the brass assays 66+ per cent. copper.

Some shippers crush to remove as much glass and wax as possible, and such lots may assay as high as 50 per cent.

ELECTROTYPE SHELLS

Often sweated before shipping, they still run high in lead, and in the past payment was not, as a rule, made for that metal. They are now at times sold for both copper and lead contents and must be sampled on that basis. On casting, the two metals will separate in two layers. The lead portion will be fairly pure lead; the copper portion will contain more or less lead and, of course, impurities.

LEAD-COVERED CABLE

Whether called "lead-covered cable" or "copper-filled cable lead," payment is made for the actual copper and for the lead plus antimony.

The cable is best stripped by hand or machine and the lead and wire portions melted separately. The former will show a low melting loss, the A. M. weight being taken as the $Pb + Sb + Sn$.

The copper portion, being stranded wire covered with insulation and coated with tar or similar material, will give a high melting loss. Shippers cannot understand why payment is not made for copper on the A. M. weight, as on the lead; obviously, copper melted and cast into a sample bar will contain considerable oxygen, to say nothing of other metallic impurities.

CARBON BLOCKS

Carbon blocks are made usually in four copper types ranging from 70 to 85 per cent. The "pig-tails," or stranded wire sometimes attached, will assay around 96 per cent. Almost all of the blocks and dust will show appreciable amounts of lead and possibly tin. They will assay from 69 to 79 per cent., rarely over 75 per cent.

They must be melted with a flux containing niter, to oxidize the carbonaceous matter, or losses in melting are apt to be high, on account of dusting.

This material may be ground in a jaw-crusher and roll-crusher but this is not advised, because, unless extraordinary care is taken in cleaning the apparatus, it might result in salting some other samples. The fine powder is not necessarily dusty of itself.

BRONZE POWDER

This material is so fluffy that it causes a great amount of trouble. It flies about and sticks to everything and should not be handled near other lower grade stuff.

AUTOMOBILE RADIATORS

Automobile radiators are not sampled but are sold on weight less iron, which is in the water connections, plates, strips, etc. Some refineries have their own list of iron deductions for radiators, as does The National Association of Waste Material Dealers. The iron deduction will range from 2 to 20 lb., the latter from truck radiators. Fords will show from 2 to 9 lb.

The remainder is chiefly copper, brass and dirt. The solder will average about 7 per cent. The recovered solder may contain as high as 40 per cent. tin. Some dealers dismantle and ship the cores; others sweat to recover the bulk of the solder. The tendency at present is to use less tin than formerly in the solder, so the figure given for that metal will probably be too high for the future.

JEWELRY AND DENTAL WASTE

An entire paper could be devoted to this important and valuable material but only the phase that affects the larger smelter will be taken up here. There are innumerable establishments making jewelry and many small dental laboratories spread over the country. The waste from the floors, sinks, benches and furnaces, etc. is saved and collected by small dealers who are usually called "refiners." Combustible matter is burnt by them to ashes, which are called "sweeps."

Metallic waste, such as clippings, punchings or stampings, is usually cast into bars called "bullion." Other names are "platers' scrap" and "filled clippings." Only the low-grade type of bullion free from the platinum group will be discussed.

SWEEPS

This material is always shipped in barrels or drums, usually sealed. Shipments vary from 1 to 7 bbl., rarely more. The entire lot is spread out on a clean floor and thoroughly mixed by shoveling, coning and quartering. It is often hygroscopic, because of the presence of sodium salts from cleaning solutions, and the moisture will run from 0.3 to 1.5 per cent. A sample for moisture is best taken at the time of dumping the barrels and immediately after weighing. This sample is usually dried at the works in the presence of the shipper's representative. As a steam bath is used, about 0.10 to 0.15 per cent. of moisture is usually left. The main lot having been quartered down carefully to about 12 lb. maximum, the sample, consisting of two opposite quarters (the other two being held as a reserve), may be placed in a pebble-mill or bucked down by hand on a bucking-board and sieved through an 80- to 120-mesh sieve, preferably the latter, to remove the scales or metallics. These will rarely run over 2 per cent., as in most cases the shipper has already sieved the sweeps through an 18 to 60-mesh screen before shipping.

The sample should be weighed *before grinding* and the metallics weighed *after screening*. The fines weight is then taken by difference. On account of dusting losses, an improper ratio would be obtained if this were not done. The fines or pulp is then mixed, quartered and bottled.

The metallics is unhomogeneous in value and particle size and, being small in amount, should be scorified with an excess of lead to 20 to 100 gm. poured in a small button or slab. The slag is cleaned and the button rasped, quartered and divided into three portions.

Fines and metallics are assayed separately for precious-metal contents only. No allowance is made for base metals.

Some works, instead of taking the struck weight of two quarters, weigh out, grind and sieve definite weights such as 16, 20, 30 or 40 assay tons. This is not recommended, for while it is convenient for calculating, it is wrong in principle.

Watch-case Bullion or Platers' Scrap

This material is very valuable. Silver will run from 1 to 50 per cent., gold from 2 to 15 per cent. and copper from 50 to 80 per cent. Payment is made for all three, the balance of the alloy being chiefly zinc and nickel.

It is shipped generally in bars, the shipments rarely exceeding 13,000 oz., as that is the full capacity of the crucible used for melting. The entire shipment, after weighing, is melted with a little borax and charcoal to a clean melt. The slag is skimmed off and poured into water to remove the bulk of the remaining charcoal, then dried and reserved.

The molten mass is stirred vigorously by plunging an iron ladle up and down with a twisting motion. A small hot clay crucible is then

dipped into the metal and a shot sample taken by pouring into a pail of water in which a wooden board rests. The hot metal is thus spattered under the water, the object being to make as little "matted" shot as possible. The very fine shot should be screened out after drying and the very coarse picked out, only the medium size, about 18 to 40 mesh, being used at one refinery, and $\frac{1}{8}$ to $\frac{1}{4}$ in. at another. The coarse assays the same but is awkward to handle at the balance: the fines will carry any slag or dirt inadvertently carried over from the surface of the melt, and should not be used for assay, as it also has a greater tendency to oxidize, by reason of the zinc present.

The metal is ladled out into bars and weighed, and the slag reserved as described above, is thrown into the crucible. The heat is raised and the pot sweated. The metal recovered is poured out, cleaned of charcoal and the total metal recovery weighed. The assay is figured on this after-melting, or A. M., weight. The treatment charges may be based on the before-melting, or B. M., weight.

A long series of experiments initiated by this laboratory and carried out some years ago at one of the refineries proved that, even on the highest grade material, no segregation troubles occurred provided the melt was thoroughly mixed, as described above. It was feared that the combination of high gold, zinc and a high-melting metal—nickel—might result in an erroneous figure if the sample was dipped from near the top. The assays of samples taken at intervals from the bottom to the top by this method showed accordant results.

Small bars, however, weighing only a few hundred ounces or less may be drilled in six holes diagonally across the bar, drilling through each time. It is very difficult to pour clean enough on a small weight to obtain a true A. M. weight, so a melted or shot sample is not always taken. The last method gives a more homogeneous sample, however. As these small bars often contain large amounts of platinum metals the relative accuracy of the two methods should be ascertained by a series of carefully controlled experiments on actual shipments.

ACKNOWLEDGMENT

The author wishes to express his thanks for the hearty coöperation extended to him by many while he was preparing this paper.

DISCUSSION

T. A. WRIGHT.—On page 678, I want to add one point: Often when drillings are taken from ingots such as are cast from melted samples, they are not ground, and there is ordinarily no necessity for it, but in large and carload shipments, handling valves, ingots and things of that kind, the samples should be ground or the results will be indeterminate. Great care must be taken in tagging and marking, and stamping the bars is especially important; that is, in relation to the melted samples. I suppose at

least 75 per cent. of the samples taken on copper scrap and on the other metals are melted. The weights before and after melting are very important and should be checked. More trouble is caused by clerical errors than by anything else.

The preparation of the samples is the all-important thing, and this is going further than what I said in regard to size of sample. No matter what scheme is used, it is governed by these factors, by the facilities that are at hand, by the weight and approximate value of the lot, and by the size and the character of the material; so that really such methods as may be given here are merely outlines of practice which must be modified many times to meet the particular situation that has developed.

W. J. BROWN, Brooklyn, N. Y.—Mr. Wright has particularly pointed out that the complexity of secondary metals makes the taking of the sample a matter of vital importance to the chemist. The work of the chemist is of little value if his sample is not representative of the original material. To leave the taking of a sample to personal selection makes sampling simply a matter of judgment. Unfortunately, many materials are of such a nature as to render other methods impractical.

When in the process of quartering, large pieces are broken down to proper particle size, returned to the sample, mixed and quartered, it is important that proper particle size be controlled by the amount of material being handled and that the quantity of sample submitted to the laboratory be controlled by particle size.

Separating into several parts either by sieving or by selection with the consequent weighing of each part increases handling charges. Dividing the "assay" into parts such as a bar and slag increases the laboratory cost. Should tin, lead and antimony be desired, it is necessary not alone to determine those metals but also copper, iron and arsenic, which may be present as impurities, and increasing the number of parts multiplies the analytical work to that extent. When the lot represents a small shipment, sampling and laboratory costs make an item to be reckoned with.

The many varieties of scrap on the market and the complexities of their compositions call for the exercise of judgment on the part of both sampler and chemist. Mr. Wright has made a valuable contribution to the secondary non-ferrous metals field in pointing out the difficulties of handling this class of material.

E. H. LAWS, New York, N. Y. (written discussion).—Mr. Wright is to be congratulated on the writing of a valuable paper on a very difficult subject.

In connection with the sampling of copper-bearing scrap material, I submit the following notes on possible improvements in practice:

It is evident that copper-bearing scrap material is most difficult to sample, owing to the variation in the value of individual particles and the high melting point of the metallic pieces. Assuming a shipment which is representative of most of the material received, it will contain metallics varying in value from pure copper to metal of no value, or even to a minus value to the copper refiner. The difficulty in sampling is increased by the variation in size of the metallic parts and because of the presence of moisture and combustible matter, such as grease, dyestuff residue, crude oil, sawdust, paper and rubber. In order to get accurate results it is obviously necessary to cut out large amounts for samples and these notes apply to the handling of such large samples, which may reasonably vary in weight between 100 and 1000 lb., according to the size and character of the shipments.

1. *Drying Tests.*—With steam-heated compartment with some controlled circulation of air and with special trays or buggies, it is practicable to dry large samples at nominal expense. This has been done with 1000-lb. ore samples in lead-smelting practice in order to speed up and make more accurate the further reduction in size to laboratory pulps, and with most successful results. In determining the value of a shipment, the moisture content is of prime importance. If a large sample is taken,

the moisture determination made can be relied on to a far greater extent than that made on the usual small grab sample. The determination should be checked by further drying the sample of the fines as it is cut down for the laboratory. In addition, the material is put in proper condition for further sampling operations. No expenditure for sampling can be made which will yield more benefit and valuable information per dollar spent than that for drying large samples. The results are convincing to both buyer and seller.

2. *Burning Tests.*—Nearly all scrap-metal material contains some combustible matter. For example, in dyestuff residues, the combined moisture and combustible matter may reach 66 per cent. It is evident that an accurate determination of the combustible matter or moisture plus combustible matter may be of greater importance in showing what the material is worth. Drying puts the sample in good condition for burning and these tests can be carried on best in a small cast-iron or steel kettle, with proper setting and with hood for taking away the smoke and fumes of grease and acid. There should be provided convenient storage for samples and floor space for cutting down the fines produced. With a small battery of such sampling kettles, the operating cost, which is chiefly for labor, can be kept at a very reasonable figure. It is apparent that the cost for floor space and equipment is low.

3. *Rejection of Worthless Metal.*—Any lead alloys or other metal fusible at low heat which separate in the kettle can be segregated. Any worthless metal which can be detected by inspection can be picked out. Scrap iron can be removed with a magnet. A hand electromagnet with control switch is suitable for this work. It will operate in the same manner as a large lifting magnet and save expensive labor, besides making a better separation.

4. *Grinding.*—After preparation of a sample as suggested, it is in first-class condition for grinding preparatory to separation of coarse metallic pieces from oxides and other earthy material which can be ground fine. For this grinding a ball-mill is indicated and has been tried out. The design must be special in that it must be possible to easily discharge the entire contents of the mill. The metallics, of course, come out clean and burnished and the fines ground to practically any fineness desired. The separation between coarse metallics and fines is sharp and after passing a suitable screen to hold back metallics, the fines can be cut down directly to laboratory pulps.

5. *Melting.*—If the metallics obtained are too large in amount for a convenient melt, they can be fairly divided by quartering, after shearing the large pieces. It is evident that the melting operation will be quite different with clean copper, brass and bronze from that in which oxides, dirt, scrap iron and other miscellaneous material must be fluxed or matted. Probably the best furnace for melting is the ordinary coke-wind furnace with fan blast and ample stack, which was used by the Nichols Copper Co. at Lindale. The high-frequency induction electric furnace, using crucibles, would be suitable because of speed and good working conditions, but the cost of the power equipment for a furnace to handle 50-lb. samples is rather high at present. In connection with melting, it should be remembered that while the metallics can run to 100 per cent. of the sample, they ordinarily form a very much smaller percentage. Also, there is no necessity for melting, for sampling operations, any material that can be crushed fine.

All of the procedure, together with the recording of the various weights, can be carried on in the works as matters of regular routine and with accuracy. The sample mill furnishes a clear record of the results on each lot and this, together with an inspection report on the physical character of the material, gives a great deal of information before assays are made. This information is often of the greatest advantage in checking back.

The sampling of lead-bearing scrap is similar to that of copper-bearing material, but the melting operation is easier; in fact, no crucible work is necessary, nor is it

advisable. I believe that sweating to metal and dross is preferable. The necessity of working with large samples is equally great, because of the varying character of the materials in one lot. The moisture content is extremely important; for example, the moisture and acid in scrap battery plates can easily range between 2.5 and 12.5 per cent.

The best method in my opinion for sampling scrap battery plates is that developed by the Pennsylvania Smelting Co. Briefly, in unloading, each fifth or tenth shovel is reserved for sample, and this amount is further reduced by reserving each second or third shovel, making the final sample 1000 to 1200 lb. The net wet weight of this sample is taken and it is stored until it can be worked. On treating in a small kettle, the moisture and acid can be expelled, the separators, and other combustible matter burned, rejected metal picked out, the metal melted down and the fines (mostly lead oxides and sulfates) skimmed off without being slagged. The metal is cast into pigs, after a sample bar has been taken. The fines are coned and quartered to 40 lb., which goes to a copper mill, is riffled and the small sample sent to a disk grinder. These operations separate the large sample, at small cost, into metal, rejected metal and fines and determine the loss. The metal and fines are put into shape for accurate sampling and, with all weights available, composites representative of the lot can be made up in the laboratory for metal determinations.

E. FITZPATRICK, New York, N. Y.—Mr. Wright says it is not necessary to take a sample of the slag from the clean metal melts, but we have found that we are taking a great chance if we discard any slag. When we first started melting these scraps, we did discard all the slag, but several times we threw away slag that afterwards was proved to contain 3 or 4 per cent. of copper. In the last few years, we have sampled and analyzed every slag.

I agree with Mr. Wright that it is very much safer to grind the samples; there are likely to be some pieces of foreign metal present, such as steel or perhaps some lead. A 20-gm. sample cannot be homogeneous unless it is ground to pass a 20-mesh screen. That is our practice.

Of course, theoretically, mill sampling of ashes and material of that kind is the best way, but we have proved that hand sampling is equally good; in fact, in some ways it is really better, because the taking of samples can be watched from the beginning to the end and there is no chance of contamination. We made some tests last year on brass ashes and skimmings. We took three of each, and, as a regular sample, selected every tenth shovelful; then as we went along we took every fifth shovelful and called that the duplicate sample. In working those samples down all the way through, they checked within 0.3 to 0.4 per cent. on the average. That satisfied us very well on the hand sampling.

One objection to the mill sampling is that the mill must be thoroughly cleaned after each milling, as there may be a large metallic portion of rich material in some of the corners which might be picked up in a later procedure.

C. S. WITHERELL, New York, N. Y.—Referring to the seventh paragraph of the chapter on Melting Equipment and Practice, wherein the author says that "the drillings should be mixed carefully before bagging, but it is rarely necessary to grind them," I wish to partly confirm and elaborate upon Mr. Fitzpatrick's remarks.

If the metal is not too hard and the A. M. bar is flat and not too thick, a sawdust sample, which is excellent, can be easily made; such sample seldom holds together as unground drillings frequently do, consequently a thorough mixture is easily obtainable without much extra preparation. The saw cuts should be equally spaded throughout the length of the bar and should extend exactly halfway across if it is desired to keep the A. M. bar intact. For lead and equally soft metals a hand sample-punch may be

used, in which event the punch should be driven an equal number of times from top and bottom of bar.

Drilling is the favorite, fastest and most widely applicable method for sampling bars, pigs, cakes, etc. of metal harder than lead, but frequently, if the metal lacks brittleness, the drillings appear as spiral shavings which entangle with each other and thus prevent adequate mixing; under this condition grinding has decided advantages.

As the author states, drillings should be taken from all portions of the bar; to insure this it is well to place the drillholes according to template, preferably with "checker-board" layout. This procedure is particularly advised for A. M. bars derived from non-alloying mixtures of metals which, consequently, are far from uniform in composition. A favorite size of drill is about $\frac{1}{2}$ in.; larger sizes are slower and smaller sizes break easily.

Grinding of copper-bullion drill samples is standard practice at all copper refineries. It is common to use a small grinder of disk or cone type, with chilled toothed grinding surfaces designed to tear the product with little or no attrition when set sufficiently coarse. Usually the ground shavings are first produced in flake form, but, at least in one make of mill (the "Hance" mill handled by The J. H. Day Co.) the flakes can be rolled up into fine shot by simply running the mill backward for the final pass. This will make a thoroughly mixed sample of such nature that the whole quantity ground can be accurately cut down and divided for the retained (bagged) samples, and also insures that the subsequent sample weighed out for laboratory determination is entirely representative of the whole drill sample produced.

Due to the extreme segregation of the precious metals in copper bullion, it is common to grind the whole or aliquot part of the drill sample until all passes through a specified mesh (usually 20 mesh) and then to separate the fines that pass through a specified finer mesh (40 to 60); the coarse and fine parts are weighed separately and then may be proportioned accordingly on the analytical scale pan or may be assayed separately and the combined assay calculated. With metal devoid of precious metals, it would seldom be warranted to pass all of the retained sample through a specified mesh as described by Mr. Fitzpatrick; but if the A. M. bar contains slag or other friable matter it may be well to screen out the fines and handle in the same manner as is commonly done with copper bullion.

A mill of the type mentioned is not costly and it requires only a few minutes and very little additional expense to put the drillings through the mill two or three times; the thorough mixing resulting therefrom would of itself warrant the extra manipulation.

T. A. WRIGHT (written discussion).—The word "rarely," to which Mr. Witherell alludes, was poorly chosen; although more of such drillings have been assayed "as is" than as ground. The author agrees with the principle; the thought in mind was that many lots of scrap weigh from $\frac{1}{2}$ to 3 tons, which is a small amount on which to spend time or money that may not be justified. However, money spent in the preparation of samples may be returned with interest in the laboratory.

F. F. COLCORD, New York, N. Y.—Are the samples always coned and quartered down?

E. FITZPATRICK.—Always.

F. F. COLCORD.—Has the ridge method ever been tried instead of coning and quartering? In coning and quartering the sample, there is always the question as to whether the right amount of fines fall evenly throughout the cone and especially when the cone is worked down. Do you pull the apex one way or another?

Years ago in the sampling of the silver ores from the Cobalt district, there was a difficulty in that much of the value was in rather coarse metallics. It was necessary

to find a means that would prevent the throwing of the apex of the cone in one or another quarter. The so-called ridge method was therefore devised.

The sample might be anything to start with; say a fifth of the original ore was taken out by shovel sample and piled in a ridge, then, starting at one end of the ridge, the material was shoveled to the right and to the left, forming two ridges. These ridges were thrown back into a single ridge, then one shovelful was thrown to the right and one to the left until the sample was halved. One of the halves was divided by the same method, giving two quarter samples.

E. FITZPATRICK.—I am afraid the metallic would be too coarse.

T. A. WRIGHT.—Secondary metals today are sold on a very narrow margin of profit and handled, as I see it and well believe, by the refinery on a very narrow margin, so that we try at all times to keep the sampling at a minimum cost. The slag question depends somewhat on the difference in practice; one refinery will add considerable flux, another will not. If an ordinary No. 2 wire or No. 2 copper, heavy, clean brass, or something like that, is taken to a copper refinery, because it has aluminum in it and the brass foundry will not take it, our experience has been that the amount of slag is very small.

I know the Nichols Copper Co. is very particular about the slag, and I have often wondered why the expense seemed justified, because I have seen cases in which the correction in the analysis was 0.07 and 0.08 of a per cent.; within the limits—far below the limits, at which a split could be made.

In regard to grinding the drillings, I had in mind there also our experiments over a long period of time in the higher grade material in which we have been running 2-gm. portions against 40-gm. and finding excellent checks.

As for the mill sample, I think that is something for the future to bring out as to its efficiency. I am mentioning it, but not endorsing it. I think it has possibilities, yet I think there are faults in regard to cleaning which complicate it. It is absolutely necessary for the large metallics to be taken out before the sample goes to the conveyor.

C. O. THIEME, Detroit, Mich.—What is done in the refining, or rather in the analysis of *terne* plates and tin-plate drosses, particularly wet dross of which a sample is sent to the laboratories and washed through by decantation? How does the umpire or the referee analyst handle the soluble losses of the tin and how does he account for it?

T. A. WRIGHT.—That particular material is one of the things we dread to see come into the laboratory, and all too often we receive only a small sample, an 8-oz. bottle, or something like that. We try to get it down to a 2-qt. jar, which is mixed up in a sort of rule-of-thumb way in a big crock, stirred, and allowed to settle and decanted off. It must be evaporated down, which is a very tedious operation. We do not find much tin in the solution, as a rule, but tests should be made for it.

Classification and Preparation of Non-ferrous Scrap Metals and Alloys

BY H. F. SEIFERT,* EAST PITTSBURGH, PA.

(New York Meeting, February, 1928)

THE classification and preparation of non-ferrous scrap metals is a subject of interest to every individual and corporation that employs in its processes of manufacture non-ferrous metals and alloys and accumulates in such manufacture scrap from these materials for disposition in the form of turnings, borings, short ends, punchings, clippings, grindings, washings, etc. All too frequently the disposition of such scrap is left to individuals who have no knowledge of the subject either from a metallurgical or a commercial standpoint, or both. Much money is thus lost which with a little more intelligent effort might be saved, and in this day of fierce competition and small profits such an opportunity cannot be ignored.

The *Mineral Resources of the United States* for the year 1925, the latest issue available (Part 1, page 221), gives the secondary non-ferrous metals of certain classes recovered in the United States for the year 1924 to 1925 as shown in Table 1. The figures are tabulated simply to give the reader some idea of the scope of the secondary non-ferrous metal industry. Approximately 900,000 tons of an annual value of \$244,000,000 were recovered in the year cited. In 1916 (again using the *Mineral Resources of the United States* as authority) the tonnage reclaimed was approximately 632,000 tons and the value, because of the high prices for metals prevailing at that time, amounted to \$265,000,000.

It is not the purpose of this paper to discuss smelting and refining operations or the feasibility of an organization, primarily engaged in some other activity, conducting smelting and refining operations to convert its own non-ferrous scrap metals and alloys. The classification and preparation of these non-ferrous materials is a preliminary step, regardless of what subsequent operations the material may pass through or where these operations may be conducted. For that reason the subject can be readily discussed without any reference to subsequent activities.

Space must be provided, with suitable handling facilities, scales and the necessary storage bins where the material may be accumulated. The scope of the activity, the nature of the industry and the tonnage handled will determine, in a large measure, what preparation, if any, it may be desirable to give these scrap materials to put them in the best marketable condition. By preparation is meant largely what, for the want of a

* Assistant Superintendent, Westinghouse Elec. & Mfg. Co.

better term, might be characterized as the mechanical preparation—such as the removal of insulation, oil, grease, etc., magnetic separation, baling for convenient handling and storage and operations of a similar nature. An alligator shear, a magnetic separator, a baling machine and a suitable outdoor space for the burning off of insulation, grease, etc., are very desirable additions to any salvage plant; although not absolutely essential if the tonnage is not sufficient or is not of a nature to justify this equipment.

TABLE 1.—*Some Secondary Non-ferrous Metals Recovered in the United States for the Year 1924-25*

Material	Short Tons	Value
Copper, including that in alloys other than brass. . .	250,600	\$ 71,170,400
Brass, scrap remelted.....	242,300	56,270,800
Lead as metal.....	112,420 }	39,477,100
Lead as alloys.....	112,460 }	
Zinc as metal.....	61,430 }	11,359,000
Zinc in alloys other than brass.....	13,300 }	
Tin as metal.....	7,950 }	35,165,400
Tin in alloys.....	23,000 }	
Antimony as metal.....	1 }	3,794,000
Antimony in alloys.....	10,839 }	
Aluminum as metal.....	17,700 }	24,816,000
Aluminum in alloys.....	26,300 }	
Nickel as metal.....	191 }	1,518,000
Nickel in non-ferrous alloys.....	2,109 }	
Total.....	882,600	\$243,570,700

In an organization such as the electrical equipment business with which the writer is connected, the quantity of non-ferrous scrap materials is a large item involving considerable money value. The classification or grading is probably a little more elaborate than would ordinarily be required, because of the many different sources from which these non-ferrous scrap materials originate and because of the complexity of the electrical equipment industry. The plan has, however, stood the test of time and is given herewith in full simply as a matter of illustration. It can be simplified as conditions require and a suitable plan can be worked out for each activity.

The classification grades, with brief descriptions and a column for the credit allowed (based, of course, on the market quotations) are given herewith.

CLASSIFICATION GRADES OF SCRAP METAL

Grade	Description	Credit Allowed
1	Clean copper short ends, etc.	
1-B	Clean copper tinned all over.	
1-C	Brazed copper end rings.	
1-D	Insulated tinned copper wire.	
1-F	Molded commutator scrap.	
2	Insulated clean copper wire.	
2-A	Dirty copper sweepings, wire.	
2-B	Barc copper-tinned ends.	
2-C	Insulated copper-tinned ends.	
3	Heavy copper turnings.	
3-A	Fine copper millings.	
3-B	Copper turnings—Serial 55797.	
4	Copper-oxide scale.	
5	Copper sulfate (bluestone).	
6	Sheet brass and short ends.	
6-A	Yellow-brass turnings.	
6-B	Heavy-sheet rotor brass.	
6-C	Yellow-brass sweepings.	
6-D	Mixed brass turnings with aluminum.	
7-A	No. 2 alloy turnings.	
8-A	No. 3 alloy turnings.	
9-A	No. 4 alloy turnings.	
10-A	No. 5 alloy turnings.	
11-A	No. 6 alloy turnings.	
12-A	No. 8 alloy turnings.	
13-A	No. 26 alloy turnings.	
14-A	No. 31 alloy turnings.	
15	Brazing spelter dross and short ends.	
16	Low-tin mixed brass turnings.	
16-A	High-tin mixed brass turnings.	
17	Dirty sheet brass, etc.	
18	Phosphor-bronze solid scrap.	
18-A	Phosphor-bronze turnings.	
19-A	No. 7 alloy turnings.	
20-A	No. 9 alloy turnings.	
21	Clean sheet-zinc scrap.	
21-A	Dirty sheet-zinc scrap.	
22	Misc. mixed brass castings.	
23-A	Fine die-casting cuttings.	
23-C	Fine die-casting dross.	
24	No. 27 alloy scrap castings.	
25	No. 28 alloy scrap castings—clean.	
25-A	No. 28 alloy scrap castings—dirty.	
26	Heavy die-casting dross ingot.	
27	Scrap lead.	
27-A	Lead and seventeen alloy dross.	
27-B	Scrap battery lead.	
27-D	Scrap No. 33 alloy.	
28	Scrap lead foil.	
29-A	Pure tin dross.	
30	Nickel-sheet scrap.	
31	RA alloy scrap castings.	
33	Good scrap aluminum.	
33-A	Aluminum turnings.	
36	Mixed aluminum turnings.	
37-B	Aluminum dross.	
38	No. 14 alloy scrap bearings.	
38-A	No. 14 alloy dross.	
39	Heavy solder dross.	
39-A	Light solder dross.	
40	No. 25 alloy solid scrap.	
40-A	Clean No. 25 alloy turnings.	
40-B	No. 25 alloy dross.	
40-C	No. 25 alloy turnings with iron.	
41	Foundry washings.	
42	Heavy foundry scrap.	
43	No. 1 emery grindings.	
43-A	No. 2 emery grindings.	
43-C	Mixed emery grindings.	
44	Electrotype metal scrap.	
45	German-silver scrap.	
46	Monel-metal scrap.	
48	Dirty mixed turnings.	
57	Scrap valve metal.	
58	Copper plated sheet steel.	
65	Tinned sheet steel scrap.	
67	Manganese copper scrap.	

CLASSIFICATION GRADES OF SCRAP METAL.—(Continued)

Grade	Description	Credit Allowed
68	Mixed lead and tin babbitt turnings.....	
30-A	Nickel wire from radio bulbs.....	
33-B	Aluminum foil.....	
69	Serial No. 60011 scrap.....	
46-A	Monel-metal turnings.....	
1-A	No. 1—No. 29—No. 30 alloy scrap castings.....	
7	No. 2 alloy scrap castings.....	
8	No. 3 alloy scrap castings.....	
9	No. 4 alloy scrap castings.....	
10	No. 5 alloy scrap castings.....	
11	No. 6 alloy scrap castings.....	
12	No. 8 alloy scrap castings.....	
13	No. 26 alloy scrap castings.....	
14	No. 31 alloy scrap castings.....	
19	No. 7 alloy scrap castings.....	
20	No. 9 alloy scrap castings.....	
34	No. 11 alloy scrap castings.....	
35	No. 12 alloy scrap castings.....	
37	No. 32 alloy scrap castings.....	

It is, of course, one object of the classification plan to segregate, and to keep segregated, materials that depreciate in value when mixed, and frequently are rendered almost useless. Every secondary smelter knows, for example, the very deleterious effects of aluminum in brass, and the importance, among other things, of keeping aluminum turnings clean in order that maximum recovery may be obtained from the subsequent melting operation—so clean, in fact, that it is frequently customary to treat such aluminum turnings with gasoline to remove oil, grease and other foreign substances. The writer has in mind a babbitting activity, where in addition to a large volume of tin-base babbitting some lead-base babbitt work was being done from time to time. It was almost impossible to maintain the proper segregation of the turnings, drosses, etc., of the two materials—so much so that it was found profitable to substitute tin-base babbitt for the lead-base babbitt, simply to avoid contamination in the drosses, skimmings and turnings.

Some years ago the writer had occasion to melt some grindings from the grinding-wheel operations in a brass foundry. These grindings were different than any heretofore received, in that the yield was much lower and it was extremely difficult to melt them at all even after considerable heat application. It was discovered that the exhaust from a recent sand-blast barrel installation was connected to the exhaust from these grinding wheels, with the result that much fine silica was introduced into the grindings, making the tonnage handled unduly large for the yield obtained and increasing the time of the process considerably because of the infusibility of the silica. The simple expedient of connecting the exhaust of this barrel with the exhaust fan of the remainder of the sand-blast equipment corrected the conditions. Many similar conditions and experiences might be mentioned.

The classification plan assigns each material its proper place and permits the cost clerk to assign the credit to the manufacturing department

where it belongs. When a penalty is exacted in the form of lower credit value for inferior grades of material, effort is soon made to rectify the condition.

It is impossible to expect the foreman in the manufacturing section or the man at the tool to possess much knowledge of the secondary-metal business or the values involved. For that reason the individual in charge of the reclamation work, or salvage department, as it is frequently called, must carry on an educational campaign among the foremen, group leaders and others in the manufacturing departments in the activity in which he is particularly interested. This he can best do by personal contact from day to day and week to week. A logical place for segregation of materials is at the machine tools where they are produced, and frequently that is the only place where such segregation can be accomplished. Hence the necessity for instructing the men in the manufacturing departments and the desirability of the overseer of this salvage work being in close contact with the manufacturing activities. This is quite essential to the success of proper classification, but once inaugurated and functioning, it requires little effort other than general supervision. Even in a large plant handling a very considerable tonnage from many different points of origin, it operates with simplicity and dispatch.

Suitable containers in the form of tote pans, cans, etc., must be provided in the manufacturing departments in which the scrap is deposited as made. When these are full they are shipped to the reclamation department with a tag attached specifying the department from which shipped, the grade number as indicated on the classification schedule if the grade is known, and the reason for scrapping. On receipt at the salvage department, the grade is recorded on the tag, or checked to be certain that it is correct if the department from which the material was shipped filled out this item of information. It is essential that the man performing this work should have a thorough knowledge of the job and the various activities throughout the organization which contribute scrap non-ferrous metals to the salvage department for reclamation. The gross, tare and net weights are also recorded on the tag and the latter then turned over to the cost clerk for pricing, in order that proper credit may be extended to the section sending in the material. Having the weight and the proper classification and the credit per pound allowed for any particular period of time, it is, of course, a simple matter to extend the credit on any particular lot or shipment.

The removal of insulation is generally desirable because in any sale of scrap material insulation must be allowed for; in any case the insulation must be removed sooner or later if the copper is to be used in the form of copper bales. The baling of scrap metals is often desirable in order that handling and shipment may be simplified and expedited and where the tonnage is of sufficient volume baling equipment pays. A magnetic

separator is often a profitable investment for the removal of iron from turnings and borings, as by this simple operation it frequently puts such turnings and borings into good merchantable condition at a minimum of cost. An alligator shear costs comparatively little but performs much useful work in a variety of ways. Not only is it used to cut up material of all types and shapes into pieces convenient to handle but scrap stock can frequently be utilized to much better advantage if objectionable pieces or appendages can be readily removed. Tinned or soldered ends on otherwise good electrolytic copper is an illustration. Suspension castings and fittings on otherwise clean electrolytic copper scrap in the form of trolley wire is another example. Many more such instances might be cited.

The classification and preparation of non-ferrous scrap metals and alloys is not a difficult task—in fact, it is a very simple one. Because of the value of the materials involved, the desire to get maximum salvage value out of them and the opportunity afforded for handling the activity on the same basis that any other activity in the plant might be conducted, the subject is worthy of the attention and consideration of every shop executive using non-ferrous metals and alloys and having salvage of these materials to contend with.

Modern Non-ferrous Secondary Metal Producer

BY DON C. BLACKMAR,* DETROIT, MICH.

(New York Meeting, February, 1928)

THE production of non-ferrous secondary metals has become a large and important industry in the United States, and deals with practically every type of manufacturing concern. Its business is unique in that it generally buys from its customers as well as sells to them, whether they are individuals, cities, corporations, or the United States government. Its operations are of vital importance to the success and prosperity of many of the nation's most important manufacturers; yet there are few industries about which less is generally known by those outside it, whether concerning the magnitude of its operations or the details of its actual technique.

The industry itself is to blame for this meager publicity, because its technical men have made few attempts to openly exchange ideas, in spite of the excellent examples set by the iron and steel or the copper and brass industries. Whether this is due to the ancient shroud of secrecy generally supposed to cover smelting operations, or because its technical men actually felt that the industry was too puny to be interesting, is hard to say.

This paper will consider its subject in a general way, attempting to show something of the size and importance of the industry, as well as its fitness to do its work well. Attention will be called to the sound economic reasons for the handling of non-ferrous wastes by specialists, and to the often unseen losses of metals and labor which occur when manufacturers reclaim their own metallic wastes.

MAGNITUDE OF THE MODERN INDUSTRY

No particular thought is given to the kitchen accident whereby a ruined saucepan is sorrowfully tossed into the ash can, yet it is a fairly safe guess that within a month this saucepan, together with hundreds of its fellows, will again be in service, perhaps in an automobile crankcase, or in an electric vacuum sweeper. It is by this conversion of the useless into the useful, whether from home or large manufacturer, that the secondary tonnage is built up.

* Superintendent and Metallurgist, Great Western Smelting & Refining Branch Federated Metals Corporation.

Table 1 shows the production of the important non-ferrous secondary metals for the year 1925. It was compiled from the figures of the U. S. Geological Survey and the American Bureau of Metal Statistics, as published in the 1927 edition of Metal Statistics of the American Metal Market.

TABLE 1.—*Recovery of Non-ferrous Metals in the United States during the Year 1925*

	POUNDS	POUNDS	APPROXIMATE AVERAGE VALUE
Copper: recovered as ingot.....	367,400,000		
Recovered in alloys not brass.....	133,800,000		
Recovered in brass scrap.....	339,220,000		
Total secondary copper production....		840,420,000	\$115,305,624
This is about 50 per cent. of the 1925 primary production.			
Tin: recovered as pig.....	15,900,000		
Recovered in alloys.....	46,000,000		
Total secondary tin production.....		61,900,000	\$ 35,165,400
This is about 41 per cent. of tin deliveries in U. S. 1925.			
Lead: recovered as pig.....	224,840,000		
Recovered in alloys.....	228,920,000		
Total secondary lead production.....		453,760,000	\$ 36,300,800
This is about 34 per cent. of the 1925 primary production.			
Zinc: recovered by redistilling.....	78,362,000		
Recovered by remelting scrap.....	44,498,000		
Recovered in brass scrap.....	106,600,000		
Recovered in alloys not brass.....	26,600,000		
Total secondary zinc production.....		256,060,000	\$ 15,363,600
This is about 22 per cent. of the 1925 primary zinc production.			
Aluminum: recovered as pig.....	35,400,000		
In alloys.....	52,600,000		
Total secondary aluminum production....		88,000,000	\$ 17,600,000
This is about 42 per cent. of the 1925 primary production.			
Antimony recovered in alloys.....	21,680,000		
This is about 100 per cent. of the 1925 antimony imports.....			
		21,680,000	\$ 2,168,000
Total secondary copper, tin, lead, zinc, aluminum and antimony.....		1,721,820,000	\$221,903,424

The year 1925 was uneventful and fairly typical of a normal prosperous period. The weights in the table, therefore, may be considered representative, although their accuracy may be open to some question as to completeness, since they are compiled largely from questionnaires. The figures may be very misleading without some study, because as far as possible they represent all secondary metals recovered or reused, whether by metal-goods manufacturers of all kinds, or by smelters strictly. This secondary metal is working capital, or metal in constant circulation, and the tonnage remains fairly constant from year to year. Only huge exports of scrap, or a very bad business depression can cause any particu-

lar decrease in this tonnage during one year, while a marked increase in tonnage will be found for any 5-yr. or 10-yr. period.

At first thought, it might appear rather startling to the primary-copper producers to know that the secondary production is almost half their own production. However, this tonnage can hardly be considered competitive, as it occupies a more or less fixed domain, not ever to be replaced by primary metal. Surely no one would be so unwise as to wish this situation to be different, because it is only by recovering all the secondary metals possible that the laws of supply and demand can be satisfied in years to come. There is no doubt that the secondary production stabilizes metal prices to a certain degree, and in so doing prevents excess profits and incites research among present-day primary producers to decrease costs. There is no argument as to the economic value of the producer and user of secondary metals.

CLASSIFICATION OF PRODUCERS

The producers of non-ferrous secondary metals may be roughly divided into four classes, as follows:

(1) Large centralized smelters handling but one class of material, such as copper-bearing residues in carload lots. Their practice parallels the primary producers almost exactly.

(2) Large smelters, scrap buyers and sellers, handling anything non-ferrous from 5 tons up.

(3) Large manufacturers who rerun some of their own scrap, but sell considerable tonnage to classes 2 or 4.

(4) Small dealers who buy and sell in comparatively small quantities, selling mostly to class 2. It is to producers in class 2 that this paper refers especially, and subsequent description will consider only this class.

SOURCES OF "RAW" MATERIALS

To successfully operate a large secondary smelter handling every non-ferrous base metal and alloy requires considerable capital and shrewd management. The stocks carried must be large, stored so as to be instantly available, and yet not hamper the continual daily turnover of the more merchantable metals. The equipment for handling the materials must be modern and sufficient, flexible, but not automatic, because of the extreme diversity of the materials. The raw materials, or waste metals, are derived by purchase from every type of industry using non-ferrous metals, and from other smelters or smaller dealers, as in class 4. Automotive industries, plumbers and printers, large electrical manufacturers and producers of canned milk, represent some contrasts in potential customers. It is to the small dealers, of course, that the con-

stant stream of household and small business scrap comes. They roughly assort this material, and sell to the smelters.

METAL SORTING

The classification or sorting of the metals received by the smelters is a highly complex task, and the most expensive single operation. The average plant will use about 135 different class names for lots into which the metals are sorted. Each class may be but the name of a group consisting actually of several lots. Thus a typical inventory will show about 250 different stock items, including new and virgin metals. The yellow brasses offer the best example of the complexity of sorting; Table 2 shows the classes made necessary to obtain the maximum profit from miscellaneous purchases of these materials.

TABLE 2.—*Sorting and Storage Classifications for Yellow Brass*

Number 1 brass tubes.	Gaskets.
Number 1 brass pipe.	Mixed small clippings (soldered or plated).
Clean nickel-plated tubes	Yellow brass faucets.
Soldered brass tubes and clips.	Number 1 high yellow cast scrap.
Number 1 brass clippings.	Aluminum brass cast scrap.
Leaded brass clippings.	Brazing spelter scrap.
Medium brass.	Number 1 manganese bronze cast scrap.
Light brass.	Manganese bronze cast turnings.
Old rolled brass.	Number 1 yellow rod turnings.
Leaded brass rod ends.	Yellow cast brass turnings.
Automobile radiators.	Yellow brass grindings.
Rifle shells.	Yellow brass furnace residues.
Tableware (nickel and silver plated).	Yellow brass with iron.

Each of these classes has an obvious or necessary reason for segregation. Some find ready sale back to brass-rolling mills, but the sorting must be perfect and the materials clean and new. Foundries take some classes for castings. The remainder go to manufacture yellow brass and the low-copper red-brass ingots.

The actual sorting of such materials is a combination of knowledge of the source, observation of color and shape, and laboratory tests. Large shipments of uniform materials offer no difficulties. Mixed lots must be screened through a coarse riddle, hand picked, and magneted. The hand sorting may be done while screening, and heavy brass wire riddles are used so that no interference is offered to using hand magnets. Screenings, borings, and small scrap are machine magneted, specially built double-belt pick-up machines being most efficient. The first or upper magnetic pulley of these machines is wound so as to cause the pieces of iron to reverse ends while moving to the upper belt. This shakes off any non-magnetic material, which might become tangled in the iron, and takes out practically 100 per cent. clean iron. The second magnet completes the

work, so that reasonably dry material may be considered iron-free after magnetizing on this type of machine. After sorting and magnetizing, sheet clippings, wire, etc., are bricked in a hydraulic press to convenient size. Certain classes are pressed into bales weighing around 1000 lb. and are wired and wrapped in burlap for convenient shipping. Other materials are stocked in bins according to class.

Other groups of waste materials which are treated according to the same general scheme include copper, red brass, babbitt, solder, typemetals, lead, tin, zinc, zinc-base die cast, nickel-bearing alloys, and aluminum. Any one or all of these materials may be found in receipts of a few hundred pounds or a carload. The sorters differentiate between several grades of red and yellow brass by color and fracture. Files and scrapers are used on dirty, painted or plated pieces to show color, and every casting must be closely examined for iron screws and other harmful materials.

Long experience and a wide knowledge of the current commercial practice and use of metals in every trade are the most valuable assets to supervisors of sorting. It is vitally important, for example, to know what type of casting will probably be aluminum bronze, therefore all gears, welding-machine parts, acid-tank rods and paper-mill pipe fittings, plating baskets, etc. are regarded with utmost suspicion. Manganese bronze may also be recognized by the type of casting. Different grades of sheet-metal clippings may be identified by similar knowledge, coupled with color and fracture tests. The aluminum-sheet and extruded-shape wastes are becoming complicated due to use of alloys, but by recognizing the purpose and knowing the source, together with hardness and bending tests, a very close grading is accomplished. Rapid laboratory tests are constantly made to check and establish precedents for materials of uncertain antecedents. The sorters use the specific gravity balance to check solders and other soft white metals, as well as melting and pouring tests, whereby the set of a small bar discloses the difference between a type metal and a similar composition of lead-base alloy containing copper.

The sorting of copper scrap presents no special difficulties. Elimination of iron, segregation of tinned and soldered clips and wire, bronze alloys, etc., are fairly easy. Common sense, knowledge of uses of metals, and laboratory tests, make it possible to grade all these materials very precisely. Where there is any doubt as to exactness in sorting, the lower grade is selected, or else the material goes to furnace charges.

Residues, which include all skimmings, drosses, ashes, etc., are almost wholly classified by assay or chemical analysis. The laboratory tests show the percentage metallic, analysis of metallic, acid content (chlorine), iron, sulfur, aluminum, silica, etc. These elements are considered in smelting to avoid unnecessary losses. While drosses are not exactly sorted, it is at times economical to screen and magnet some classes, so that with the fines and iron removed, contaminants may be easily picked

out. Examples of this are solder sweepings from automobile-radiator manufacturers, which may contain brass tubes, and electrotypes dross containing copper trimmings.

PRODUCTION OF SECONDARY METALS AND ALLOYS

With the large metal stocks carried by the modern smelter correctly graded, cleaned, and stored, it is obvious that the manufacture of any required metal or alloy ingot, pig, or bar, consists first of the proper selection of materials and then the application of the correct metallurgical principles to their smelting and refining. It is because of these diversified stocks that it is possible to produce metals and alloys economically, so that they may be sold at or below the new metal-market value. The fact that these alloys may be 100 per cent. secondary is no cause for alarm or censure. The ores from which many virgin metals are produced contain impurities far more harmful to the metal than will be found in the average run of scrap metals. Yet the primary smelters produce, from impure ores, virgin metals of high purity, which, properly used, will answer any modern commercial requirements. Is it not reasonable to expect that the secondary smelters have devised methods for removing harmful impurities from secondary metals and alloys, so that their finished product will also answer any modern commercial requirements? This is the function of the modern secondary smelter: to market scrap that is fit for reuse without further treatment, and to so treat unfit material that it will be usable.

COPPER INGOT

The production of secondary copper ingot, known as casting copper, is the oldest art in the secondary industry. The improvements in modern practice are largely mechanical. The materials used come from every industrial user of copper in any form, and every type of pure copper scrap goes to make up furnace charges. Furnace practice is almost identical with lake copper furnace practice, impurities being removed by blowing, and deoxidization accomplished by poling. A copper ingot having a minimum purity of 99.75 per cent. copper with a correct pitch is the ultimate product. Mechanical casting devices with molds dumping the ingots into water, to be carried by conveyors to weighing buggies, are universally used. The product is a standard commercial article of good repute.

BRASS AND BRONZE INGOT

To manufacture brass and bronze ingot the modern smelter melts in oil-fired reverberatory furnaces up to 60,000 lb. capacity. Some kinds of yellow-brass ingot and nickel-brass alloys are still made in large crucibles, coke or oil-fired, because of the constant puddling required to

melt light scrap without high losses. Charges for red ingot are made up from borings, cast scrap, bronze and copper clips and wire, and stock ingot.

The charges for refined red ingot are carefully computed and weighed before loading the furnace. During the smelting operation impurities are removed by oxidization and the use of common fluxes. Deoxidization is accomplished by poling and the use of metallic deoxidizers. After treatment, the molten metal is protected by flux coverings and the analysis checked before pouring. Mechanical or semi-mechanical pour-off devices are employed, and the hot ingots are generally dumped into a water-cooled bosh, to be removed by conveyors or by hand to weighing buggies. Ingot from properly controlled reverberatory charges will give the maximum physical properties to castings made from it. There is no reason why virgin metals should not give the same properties, but it is common knowledge among foundrymen that few melters can mix virgin metals for certain alloys and obtain maximum properties on the first pouring.

WHITE METALS OR SOFT ALLOYS

The production of finished white metals,—babbitts, solders, type metals, antimonial lead, plumber's lead, etc., is generally accomplished by remelting refined stock pigs of known analysis, adding the necessary new metals, and pouring into the required shapes. Pigs weighing from 25 to 100 lb., 5 to 15-lb. plain or notch bars, $\frac{1}{4}$ to 1 $\frac{1}{2}$ -lb. solder bars, are among the common shapes. These molds are generally water-cooled, and the smaller bars are poured two to eight at a time by multiple-spout ladles, the casters becoming very adept at this neat work. The stock pigs used for white metals are derived from graded scrap, skimmings and drosses. Borings, bearings, castings, solder joints, etc., are sweated or melted in large quantities. Impurities are removed from the molten metals in iron kettles holding up to 100,000 lb., by oxidization, which may be accomplished by blowing or mechanical agitation, by sulfuring, or by other treatment depending on the impurities to be removed. Impurities in some alloys are required ingredients in others, so that considerable economy is developed by close supervision over the classes of materials to be refined.

Skimmings and drosses are reduced in reverberatory furnaces at high temperature with suitable fluxes. The resulting metal is tapped into a holding kettle and pigged out. The slags from rich drosses are rerun with other drosses, and mattes are sometimes produced which are again smelted in cupolas. The pigs from dross furnaces are sweated or liquated in sweat furnaces with close temperature control, the constituents of lower melting point running into holding kettles, to be pigged out. These pigs are then kettle refined with the scrap materials as described above, becoming refined stock pig. The constituents of higher melting point

left in the sweat furnaces, generally rich in copper, iron and zinc, are taken out as slush pigs, to be rerun with other drosses. The desired result here is concentration in two directions, a rapid turnover into good alloy stock pig immediately usable, and a slower building up of material of high copper content from the cupola.

ZINC AND ZINC-BASE ALLOYS

The production of remelted zinc consists of melting properly graded new zinc clippings, cans, covers, linings, etc., in iron pots, cleansing with sal ammoniac, and pouring into slabs or notch bars. Iron, tin and lead are the usual impurities, but the average zinc content will be close to 99 per cent. where the sorting of scrap is carefully done, and the charges well proportioned. Zinc-base die-cast scrap is melted and treated in the same way, stock pigs being produced, which, if used for making up die-casting alloys, require large quantities of virgin zinc to reduce the constituents to the close limits required by the users. As a result, there is constantly an excess of die-cast scrap stocks, there being very little use for such mixed compositions containing several per cent. each of copper, aluminum, tin, 0.5 per cent. lead, balance zinc. The value of die-cast zinc scrap and residues is consequently very low, and will continue so until some demand is developed for these mixed alloys, or until all zinc-base die castings are made from the same specification by all die casters.

The residue from melting zinc scrap and from the industrial use of zinc alloys are not usually smelted by the class 2 smelter, but are shipped to a class 1 smelter handling only such materials. There they are treated in the way used for zinc ores, the metal being recovered by retorting. Practically all these smelters are in the districts of primary zinc smelting.

ALUMINUM

The production of secondary aluminum is still a comparatively new branch of the smelting industry. The modern tendency is toward melting in large reverberatory furnaces up to 20,000-lb. capacity, using salt and cryolite mixtures as flux or cover. Because aluminum oxide or dross is not reduced by fluxes in smelting operations, the problems are principally the prevention of its formation. By properly proportioning charges of borings, castings, stock ingot made from skimmings, screenings, and pure clippings, a No. 12 remelt ingot is produced. Special alloys to closer specifications are made from new sheet clippings with additions of copper, silicon, nickel, etc., as the case may be. Such alloys are likely to have superior sand-casting qualities and better physical properties than the same compositions made from some virgin ingot aluminum. This is probably because pure rolled and extruded shapes which have passed the manufacturers' inspection will be purer and contain less

dissolved oxides and gases than some virgin ingot which has not been remelted. The class 2 smelter generally makes small quantities of these special alloys in iron pots holding from 300 to 1200 lb., to avoid excessive melting losses. A large proportion of the class 2 smelter's aluminum sales consists of scrap for remelting purposes. The principal classes sold are clean new castings, bricked pure sheet clippings, cut molding and extruded shapes, pistons, and some alloy sheet and forgings.

The art of recovering metal from aluminum residues has not made much progress in the smelting industry. The procedure is to remove all possible oxide and dirt by dry crushing and screening, remove free iron by magnetizing, and melt the resulting metallic lumps and screenings under heavy salt and cryolite flux cover in a reverberatory furnace. The fines screened out have a very limited use and represent a total loss of aluminum content, as they are generally discarded for want of a paying recovery process.

IMPORTANCE OF LABORATORY

The smelter laboratory must necessarily be a very competent department. The routine work is largely rapid analyses of all non-ferrous alloys. Furnace and large kettle charges are held molten waiting to pour off, while the composition is checked. Purchased materials, stock pigs and special alloys require complete analysis. Methods for assaying every known non-ferrous residue must be devised, and some of these are of startling complexity. Physical tests are also part of the routine, and the microscope is used to examine metals and alloys for oxides, foreign inclusions, and segregation. The laboratory is also part of the service extended to customers, who are invited to send in samples for analysis, or problems for aid and advice. These problems may include foundry practice in brass, aluminum, aluminum bronze, or monel metal, sand testing, soldering, babbitting, die casting, corrosion, machining, or anything in any non-ferrous industry. Reports to customers are generally accompanied by photomicrographs if the problem requires them.

CONCLUSION

Constant economy is necessary if the modern non-ferrous smelter is to succeed. This is actually realized by continual close supervision, observation, and constant seeking and testing of new ideas. Experience has shown where losses are greatest, and they can be very serious even though not at all apparent to the untrained eye. An example of this is volatilization loss, which is reduced to a minimum by recovering the metals in fumes from all the smelting furnaces in Cottrell electric-precipitation installations. The precipitates are principally mixtures of zinc, tin, and lead oxides, and after removing the zinc, the other oxides are again charged to the dross furnaces.

A similar example of cost reduction consists of so preparing furnace slags that they may be sold for use in other industries. Even the aluminum-oxide screenings find occasional users in the chemical or oil-refining industries. Silverplated tableware and other silver-bearing scrap are carefully segregated and sold to refineries. Special processes are constantly devised for separating mixed wastes, such as those produced in the automotive industry, where borings from babbitt, brass, iron, wood, aluminum, solder, and zinc, may be mixed in any combination of two or three metals, and possibly soaked in oil.

The industrial plant that attempts to recover its own non-ferrous waste materials would do well to ascertain if its operations are really profitable. Very often the industrial plant obtains several products from attempted salvage of a given item; one high grade, for re-use; the rest, too low grade to bring much revenue when sold. If the uncontrolled losses, high labor costs due to lack of experience, and depreciation in value of the low-grade material, which must finally be sold, are all considered, it would probably be discovered that the operations show no profit whatever, or even considerable loss.

The secondary smelters are paying more today for non-ferrous wastes of all kinds than ever before, and selling high-grade products on a much closer margin than formerly. There can be but one answer: that the modern secondary producer is efficient and economical, and is recovering everything recoverable—getting all the value possible out of all the material handled.

DISCUSSION

E. R. DARBY, Toledo, Ohio.—There is one point which I think is very important: A great many of us are attempting to recover our own waste; perhaps we are doing it correctly and perhaps we are not. If we are not doing it correctly it would probably be of more economic importance to the country at large to sell it to the secondary smelters.

C. O. THIEME, Detroit, Mich.—As a representative of a smelter, it is not my intention even to intimate that there are not men who are capable of properly refining their own scrap, but it seems to me that the biggest point to be brought out is that the smaller plants must maintain special equipment to properly refine their scrap. In our own plant, it is necessary to group certain classifications of materials and to mix certain drosses to get the highest maximum recovery.

G. H. CLAMER, Philadelphia, Pa.—Some time ago there was organized a committee for suggesting ways and means for promoting the usefulness of the A. S. T. M. work, one function of the Committee being to bring to the attention of the public the A. S. T. M. specifications and attempt to promote their wider use. Secretary Warwick invited me to write an article for publication in the bulletin on that subject, and it occurred to me that one of the ways in which to promote the usefulness of the A. S. T. M. work was to use the specifications as a basis for market quotations. With that in mind, I looked over the manner in which the trade papers were quoting on ingot metals. I found that they were describing the products on which they were

basing their quotations in a very crude and unsatisfactory manner. For example, in their description of No. 1 composition (as it is known in the trade) they simply refer to it as "85-5-5-5." There was no indication as to what the figures refer to. Of course, we in the trade know that it means 85 copper, 5 tin, 5 lead, and 5 zinc. There is no limit given for the constituents plus or minus, and no indication of what the impurities might be and their limitations. In general, the description was, to say the least, decidedly loose. The same thing held true of 88-10-2, 80-10-10 and so on. The description in every case was decidedly meager.

I suggested that the A. S. T. M. might profitably organize a committee to investigate this subject and issue a call to the producers and consumers and the publishers of trade papers to see if it would not be possible to formulate some plan whereby these quotations might be based on more definite descriptions.

I presented a resolution at the French Lick meeting of the A. S. T. M. last June. The resolution was presented to the executive committee, and a subcommittee of the executive committee was appointed to look further into the matter. A meeting was held in New York about two months ago and as a result the subcommittee recommended to the executive committee the organization of a committee such as I had suggested. That committee's action was based on the replies received to a great deal of correspondence with producers and consumers and also the publishers of the trade papers.

The next step will be to organize that committee. I believe as a result of that work the quotations will be based on better understanding. If the present specifications of the A. S. T. M. are not entirely practical to meet the trade requirements, it will be for that committee to modify the specifications so that they will be in every way practical. Probably that is only the first step. The quotations on ingot metal may be based on more flagrant lack of description than the quotations on any other commodities, but if the A. S. T. M. specifications could be used very much more extensively as a basis for trade-paper quotations, both for wrought brass and the iron and steel products etc., there certainly would be a very much better understanding in the trade.

W. C. HIRSCH, Rahway, N. J.—Considerable progress has been made on the ferrous end of the alloy steels. The A. S. A. E. numbers have been substituted for descriptions of alloy steel and they are now so quoted. The numbers of the A. S. T. M. would simply take the place of the 85-5-5-5, which means nothing. It would be a progressive step, and a great help.

J. B. WATERFIELD, Attleboro, Mass.—General Motors, in buying ingot metal, distinctly states 85-5-5-5, lists the maximum impurities, what the metal has to stand in tensile strength, etc. If such knowledge can be brought before the general metal-buying public, it would be to the advantage of everybody.

The Contamination of Metal Scrap, Its Effect on the Value, and Suggested Means of Control

BY CARL O. THIEME,* DETROIT, MICH.

(New York Meeting, February, 1928)

INDUSTRIAL specialization has rapidly created a demand for new and better alloys. A more thorough understanding of the requirements of specific industries and the discovery of processes by which it has been made possible to utilize certain metallic elements in larger quantities, together with greater purity in most virgin metals, has resulted in a great increase in the number and variety of alloys.

This increase in the number of elements entering into non-ferrous alloy manufacture has increased the contamination in secondary metals, as received by the smelter. In order to successfully refine scrap of a much more complex nature it has been necessary for the smelter to install new equipment and to constantly search for new methods of refining as well as to improve the methods already in use. In some instances it is largely responsible for specialization in the secondary metal industry.

It is usually necessary to remove the contaminating impurities in scrap or eliminate to a degree not objectionable, no matter how introduced. In order to know what metals or elements are of an objectionable nature, the smelter must make a study of the effect of single elements and combinations of elements on many of the physical and mechanical properties, such as strength, ductility, color, hardness, casting soundness, etc.

The smelter of secondary metals must be able to utilize scrap materials of all kinds, for, sooner or later, most fabricated metal parts and the waste products formed during the process of manufacture find their way to the smelter. In addition, the smelter, in contracting for salvaged material from the producer, gets some undesirable and unusual materials. The value of secondary metals and the importance of their recovery has increased in recent years and it is no longer sufficient to recover the base metal only, such as copper from copper-bearing material, but it is essential that other elements present be recovered and converted into useful form.

This paper will deal not with the smelting and refining or separation of impurities from secondary metals but an attempt will be made to show the increased value of metal scrap when properly segregated and in a less contaminated condition. There are five principal reasons for contamination in secondary metals: New and unusual alloys, productive methods,

* Chief Chemist, Michigan Smelting & Refining Co.

carelessness, ignorance and unsuitable means of refining. Not to be overlooked is the variation in the purity of various grades of virgin metal.

NEW AND UNUSUAL ALLOYS

The contamination from new and unusual alloys is readily understood and little need be said regarding it except to mention some of the elements introduced by this means—chromium, molybdenum, tungsten, vanadium, sodium, calcium and other elements unusual to the non-ferrous alloys as usually manufactured. In addition, unusual combination of elements common to some alloys play a big part in this sort of contamination.

PRODUCTIVE METHODS

Much of the contamination in metal scrap is due to the demand on the manufacturer of metal parts for production methods in which contamination can not be avoided. For example:

Machine cuts on a metal part consisting of two or more widely differing classes of alloys such as brass and babbitt or aluminum and babbitt.

Soldered or brazed, sheet or cast parts. Under this head come the requirements of the automobile radiator industry.

Electroplated articles, including copper, brass, nickel, silver and chromium plating. This is not a complete list of the electro-deposited metals sometimes encountered.

Brass, iron and aluminum inserts in castings, as often encountered in the die casting scrap.

Iron and lead accumulation in galvanizing baths.

Copper, brass, iron or other metal dissolved in solder or tin baths as various articles are dip soldered or coated.

This type of contamination will probably increase, but as the source of such scrap is more or less constant, the tonnage is usually great enough to warrant the smelter to invest in equipment with which he can successfully treat such scrap.

CARELESSNESS

Contamination due to carelessness occurs frequently in plants producing scrap, wherein two materials of unlike nature or of different commodity classification are mixed. More consideration is now given in many plants, regardless of size, to the proper segregation of unlike material, with the thought of increasing the value. As the value of secondary metals is being brought to the attention of the right men in the industry we may expect less volume of careless contamination. Take for an example, solder and babbitt dross (whether lead or tin-base) if mixed and smelted, for in this condition the smelter cannot separate the dross. The pig metal recovered has the antimony content alone, or the copper and

antimony content increased to a degree where it directly influences the value of the dross. A penalty must be imposed upon the producer of scrap by the smelter when the copper or antimony content increases above a certain percentage or when zinc or aluminum is present.

Specifications for solder alloys usually allow but 0.08 per cent. copper and from 0.25 to 0.75 per cent. antimony, while they require the absence of zinc and aluminum. The metal recovered from mixed drosses may be microscopically free from oxides and so-called dirt, and it may contain no other impurities except arsenic or bismuth which are introduced with the virgin metal when the alloy is first made, but it is a difficult task to remove a few per cent. of antimony except by a time consuming process of liquation or by electrolytic methods. The high cost of the electrolytic methods inhibits their use in this country and when the liquation process is used, a large percentage of the once valuable tin (in the form of solder) is now in an undesirable form. The alloy contains a high antimony content together with varying percentages of lead.

The lead content of the so-called "Sweats residue" is too high to warrant its use in the incorporation of antimony into tin-base babbitt metal and as the intermediate babbitt metals find so little application, there is usually an abundance of this "Sweats residue" on the market. The tin contained has little value for there is no outlet for the product. The result is that the value of the solder dross has been reduced through contamination and, of course, the same penalties are imposed whether the cause is carelessness or otherwise.

Other illustrations of the reduction in value of contaminated scrap could be given, but this serves to show how the value is directly influenced by contamination and the urge for proper segregation in the producing plant.

IGNORANCE

Ignorance of the value of secondary metals is fast disappearing. We have evidence that even the children in the street know the value of metal foil from the number of them collecting candy wrappers, cigaret packages and the like. As aluminum foil is in many instances replacing tin on candy wrappers and collapsible tubes, considerable contamination is thus occurring from this source.

Ignorance on the part of the employee who handles scrap metal in the producing plant is largely responsible for this type of contamination. To the uninstructed new employee, or to the laborer handling salvaged material, metal is metal whether it is iron, brass, babbitt or aluminum and often many tons of material are placed in a lower commodity classification because ignorant or uninstructed employees have mixed scrap metals that are of the same color. Innumerable instances of this type of contamination have come to our attention.

UNSUITABLE METHODS OF REFINING

Smelting and refining of certain classes of secondary metal scrap should not be attempted by the uninformed or inexperienced person. The presence of some impurities will probably pass undetected and will cause no end of difficulties in the casting operation, machining of castings and finally, in service. The smelter, whose business it is to utilize scrap metals, should be in a position to refine scrap metals more properly and remove impurities or dispose of undesirable scrap wherein the smallest loss is incurred.

Proper refining of metals is a matter of great importance and involves not only metal loss, but a thorough knowledge of furnaces, their type and construction, the selection of burners, the choice of fuel, flux and slag-forming materials. Last but not least, a thorough working knowledge of the principles of physical chemistry is necessary.

Some of the more important considerations are: Oxidation or reduction and control of the reaction; and the introduction of gases from the fuel or from the atmosphere within the furnace, and of non-metallic materials sometimes objectionable, from the fuel or furnace linings. Temperature maintained during refining and time are factors of great importance. Whether we agitate a metal bath or allow it to be as quiet as possible, elimination of objectionable oxides, choice of oxidizing or reducing materials and the casting temperature are considerations not to be overlooked. Fluxing materials or slag-forming materials must be added at the right time and in the proper manner, for there are instances where the desired reaction will take place only when the flux is added just as a definite temperature is attained or if the slag is not formed too soon.

It has been our observation that attempts by inexperienced persons to utilize certain metal scrap have resulted in the contamination of thousands of pounds of absolutely good material and the loss of time and money. Even if an operation was more or less successful, the metal losses were generally greater than those occurring in the plant of the smelter, for generally the smelter is compelled to reduce metal losses to the minimum in order to operate at a profit. The contaminated metal invariably was sent to a smelter for refining or sold at a loss.

VIRGIN METALS OF HIGHER THAN NORMAL IMPURITIES

Mention must be made of the occasional finding of virgin metals whose percentage of impurities is higher than normal. Some of these metals are bought, not on specification of any particular impurity, but on the percentage of total impurity. It is not difficult to understand why these impurities are present in such quantities for the loss involved in removing the impurity from 0.10 to 0.02 or 0.03 per cent. (a percentage not objec-

tionable) is out of proportion to the quantity of impurity removed. So long as material is bought on such a basis this condition will exist and all users of the metals will have to contend with certain impurities until specifications can be written that will be more fair to the consumer. Contamination will continue to take place, as there seems to be no remedy in sight at present.

Since contamination is constantly taking place the smelter must interest himself in the real or approximate composition, depending upon the nature of the scrap offered for sale. Not only is it necessary to know the percentage of major elements in order to place the scrap within a commodity classification, but in many cases the smelter and refiner must ascertain the nature and extent of the impurities present, thus enabling him to place a true value on the commodity as well as to guide him in the proper method of refining or final disposition of the metal recovered.

As an example, let us consider the standard 85-5-5-5 composition boring. The main element, copper, may be plus or minus a few per cent. without changing the commodity price, but if contaminated with aluminum chips the value of the scrap is greatly reduced. This is but one of the many instances in which the impurities directly lower the price of the commodity because treatment of a complex nature is often necessary before the metal is of proper quality for use.

NON-METALLIC IMPURITIES

It is often necessary to determine the non-metallic material present in secondary scrap in order to reduce metal losses to the minimum. Some non-metallic solids, often organic in nature, and some gases greatly interfere with smelting and refining operations and smelters penalize quite severely as the percentages of these impurities increase.

WHAT IS AN IMPURITY?

It will be of interest to mention briefly what constitutes impurities in metal scrap or waste products containing metal. We must include all the elements usually incorporated in the manufacture of alloys, for elements essential in one type of alloy are impurities in others. The following elements are commonly encountered: Copper, tin, lead, zinc, iron, aluminum, nickel, antimony, silicon, manganese, magnesium, bismuth, cadmium, arsenic and calcium. Tungsten, chromium, molybdenum, vanadium, selenium, tellurium, beryllium and other elements are occasionally found. Gaseous elements and compounds are frequently dealt with as well as elements such as carbon, phosphorus and sulfur. Other elements or compounds occasionally interfere with the smelting and refining operation or are mechanically occluded in the recovered pig metal. Although some of these impurities are objectionable in almost every instance, certain elements or compounds objectionable in some

alloys are not objectionable in others. A few examples will serve to illustrate this point.

Contamination of 85-5-5 standard brass with aluminum has already been mentioned, for metallic aluminum is deleterious to practically all the physical and mechanical properties of the metal. However, aluminum is intentionally added to yellow brass, with general improvement in properties.

Zinc is considered an impurity in most of the light aluminum alloys but it is intentionally added to some of the aluminum-base alloys in quite large quantities.

Phosphorus is intentionally added to many of the red brass or bronze alloys but rarely to the yellow brass and is undesirable if present.

Iron is intentionally added in fairly large percentages to some brass and bronze alloys but is considered an undesirable impurity in quantities greater than 0.35 per cent. in others.

Copper is an undesirable element when present in solder metal as stated previously, but both tin and lead are added to copper with resulting favorable properties.

Antimony is intentionally added to most babbitt metals whether tin-base or lead-base, but when present in a tin and lead solder, it is usually considered undesirable.

Lead and zinc are considered impurities to be avoided in some of the high-copper alloys. The presence of lead in most of the high tensile alloys has a detrimental effect on the physical properties.

Sulfur is undesirable in practically all alloys but it is intentionally added either as sulfur or a sulfide in one or two bronze-bearing alloys.

CONTROL OF CONTAMINATION

In attempting to eliminate contamination as much as possible, the smelter has, through cooperation with the producer of scrap metals, effected much improvement. Suggestions made and followed have resulted in great savings to the seller of the scrap. Clean scrap means small loss, low cost of refining and no penalties, naturally increasing the value of the metal scrap.

Many industrial organizations maintain a salvage department, employing trained men at the head, whose duties are not only to maintain segregations of the scrap materials in the storage room, and to make proper classification, but to devise ways and means of keeping the metal scrap in the least contaminated condition as it is produced in the manufacturing departments. The clean-up men, sweepers and the like are usually under the control of the salvage men with the result that, unless contamination has occurred as under the second heading, the scrap is reasonably clean. Some of these men keep in close contact with the smelter and are advised as new problems arise.

Control of contamination could be increased if more of the firms producing scrap materials were placed on a basis as above described, for substantial gains in savings would result from clean salvaged metal scrap.

Finally, notwithstanding this contamination, the smelter and refiner of secondary metals is governed in the quality of metal produced by the specifications which he must meet. Most of the larger smelters maintain laboratories and can guarantee to produce metal according to the customer's standards. If specifications are not given, the smelter is guided in the production of alloys or metals made with secondary scrap by the metal specifications of the American Society for Testing Materials. It is hoped that these or some other set of standard specifications will be followed more closely by those issuing or revising material specifications. It is also hoped that with the use of standard specifications the number of alloy compositions intended for the same purpose will be reduced.

To those issuing metal specifications we urge careful consideration when controlling metal impurity percentages. In many instances only a small percentage of a metal is permissible, whereas five or six times as much would not injure the properties of the alloy for the purpose intended. For example, many specifications now limit the lead content in tin-base babbitt to 0.35 per cent., whereas as high as 2 per cent. would not be objectionable in most babbitt bearings. Some of the largest users of babbitt alloys are now permitting from 1 to 2 per cent. of lead in the babbitt purchased, thereby realizing a tremendous saving without sacrificing quality.

DISCUSSION

W. F. GRAHAM, Mansfield, Ohio (written discussion).—Mr Thieme's paper was evidently written to direct the attention of the user of non-ferrous metals, who is in turn the producer of the raw material for the secondary-metals refiner, to the effect of contaminations in this material and the troubles which they cause the refiner.

While the refiner is undoubtedly beset with many difficulties in handling the miscellaneous materials from which he produces his secondary metals, the organization with which the writer is connected (Ohio Brass Co.) is very well satisfied that the majority of the producers of composition brass ingot can meet a reasonable chemical specification and keep the recognized impurities (for example, iron and antimony) so low that they will not affect the quality of the alloy.

Table 1 shows specifications for two grades of composition brass ingot and the average analysis of 63 cars received over a period of two years from a number of sources of supply. These figures indicate that the specifications have been met with the exception of the zinc content and that very little difficulty has been experienced with off-analysis material. However, on the other hand, we are not at all satisfied that the average producer of composition brass ingot has a proper appreciation, from a metallurgical standpoint, of the reactions taking place in his refining furnaces. In an investigation extending over the last six months in our own plant and in plants of secondary-metal refiners, who produce composition brass ingot, we find that there is a wide variation in the quality of ingot with reference to the amount of non-metallic inclusions.

TABLE 1.—*Ohio Brass Specifications*

	Copper, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Zinc, Per Cent.	Iron, Per Cent.	Antimony, Per Cent.
No. 4 ingot.....	79.0-81.0	2.5-4.0	6.5-7.5	9.5-10.5	0.25 max	0.25 max
No. 5 ingot.....	83.0-85.0	2.5-4.0	2.5-3.5	9.5-10.5	0.25 max	0.25 max

NOTE.—Total impurities not to exceed 0.30 per cent.

Average Analyses for 1926

No. 4 ingot.....	79.0	3.4	7.4	9.9	0.14	0.12
No. 5 ingot.....	84.5	3.7	3.6	8.0	0.08	0.10

Average Analyses for 1927

No. 4 ingot.....	79.7	3.6	7.4	9.2	0.14	0.12
No. 5 ingot.....	84.2	3.4	3.5	8.6	0.11	0.11

NOTE.—Nickel has been found in some shipments up to 0.50 per cent. but is not considered an impurity.

Composition brass ingot is produced in a variety of ways. Furnace sizes vary from 1 to 50 tons and the metallurgical process may be either one of bessemerization of the so-called impurities or their removal by a fluxing treatment. It would appear to us that a uniform quality of brass ingot can not be offered to the trade until a more standard procedure is adopted by the refiners in general and the metallurgical aspects of their processes in relation to the ultimate quality of the product is given more consideration. The immediate results will be a reduction in "dirty" castings and "leakers" in the foundries using composition brass ingot.

We feel that the secondary refiner is filling an important position in industry and that the collection of so-called scrap and its conversion to a usable form is an economic necessity. Secondary metals, when produced by proper methods of refining, should equal virgin metal in performance, particularly those of brass compositions. The metal refiner should be supported in his efforts to produce a quality metal, not only by those from whom he obtains his raw material but also by those who use his product.

W. M. CORSE, Washington, D. C.—I would like to supplement what Mr. Graham has just said by adding the word nickel-silver to brass. I have had some experience recently in trying to get the proper quality, or in seeing that manufacturers received secondary metal ingots of proper quality, for what used to be called German silver, but which we now call nickel-silver. All the things he has said in his discussion about the importance of knowing the metallurgical principles, as far as brass is concerned, apply, I should say, even more to the same alloys when nickel is added.

We know a good deal more, thanks to Dr. Merica and his colleagues, about the effect of sulfur on alloys containing nickel. When we get a miscellaneous assortment of scrap of unknown history, the sulfur content is sometimes ignored and makes trouble unless people who are handling it realize the importance it plays in the quality of the resultant material. Nickel also requires unusual attention, and nickel alloys of the German silver type are becoming of increasing importance. I would urge anybody who is making secondary metals of the German silver variety to look carefully into the underlying metallurgical principles involved so that they may be in a position to furnish what the brass people are now furnishing; namely, a metal com-

parable in quality to that produced by new material. It is very important from the casting standpoint that the sulfur element particularly be taken into account and that the material which we will say contains 20 per cent. nickel, roughly, is of good quality.

Those who have tried to explain to the foundryman why he has not secured good castings or why he should be interested in making nickel-silver castings, for instance, in the plumbing fixture lines, know that proper quality is very important. The whole nickel-silver business has suffered from this one point and many people would be using nickel-silver castings today if they could get the proper quality of material and if the refiners would realize the fundamental metallurgical principles involved in its manufacture.

All nickel ores contain sulfur when they come out of the ground. In the refinery we try to reduce that to 0.03 or 0.04 per cent. When sulfur comes anywhere near nickel, it is a very easy thing to unite them; so it is not the fault of the nickel that sulfur gets into it; it is the fault of the man who puts the sulfur near the nickel.

J. B. WATERFIELD, Attleboro, Mass.—In reference to sulfur in nickel-silver, it occurs to me that the trouble may be that the sulfur has an affinity for the copper. In melting nickel silver, it has been my experience that sometimes after it has been silver plated and polished sulfur is slightly absorbed by the copper, and on a finished product we get a copper sulfide or sulfate condition rather than nickel sulfide or sulfate.

E. R. DARBY, Toledo, Ohio.—I believe there is a tendency on the automobile industry's part to allow more lead in tin-base babbitts, I know some automobile manufacturers allow as much as 1.5 per cent.; some, as much as 2 per cent. I believe there are some very reputable airplane-engine manufacturers using a lead-base babbitt, so that perhaps secondary-metal producers in the future will find they will not be held quite so low on lead content, which I think will be an advantage.

O. W. ELLIS, East Pittsburgh, Pa. (written discussion).—The concluding paragraph of Mr. Thieme's paper will excite the interest of users of babbitt. It would be interesting to know on what basis the author is able to make the statement that "a tremendous saving without sacrificing quality" can be realized by the user of babbitt containing from 1 to 2 per cent. of lead. The writer can fully agree with the statement as to saving, but is a little dubious as to the question of quality.

From a mechanical point of view, lead is considered by many to be a useful addition to babbitt, since its substitution for tin has the effect of increasing the hardness and compressive strength of these alloys at ordinary temperatures. Substitution of more than 1 per cent. of tin by lead, however, has no beneficial effect on the hardness or strength of babbitt, the hardness and strength due to this substitution reaching a maximum value at just about 1 per cent. lead. The hardening and strengthening effects are completely lost at high temperatures (75° to 100° C.), the alloy behaving as though no substitution of tin by lead had occurred. There is some evidence that lead has an embrittling effect on babbitt. Certain it is that, other things being equal, the CuSn needles in babbitt tend to crystallize in the form of very long needles when lead is a constituent of the alloy, structures being obtained such as are frequently associated with brittleness. On this account, one would feel disposed to limit the lead content of babbitt.

There is yet another reason for such action. It is because there is a tendency for babbitt to absorb lead from the solder used in tinning the bearing. Contamination of the babbitt on this account may be an important factor in the life of the bearing. It is not impossible for the lead content of a lead-free babbitt to be increased in parts to as much as 0.5 per cent. as a result of contamination by the tinning solder. Such contamination would also occur in high-lead babbitts and still further raise their proportion of lead.

It is probable that the author has some new quantitative data regarding the effect of lead on babbitt which would lead us to change our opinion regarding this element. If such data can be published they would be much appreciated.

C. O. THIEME (written discussion).—Many specifications allow from 1 to 2 per cent. lead in babbitt and "for the purpose intended" the bearings are proving satisfactory in service. The author does not believe automobile manufacturers would sacrifice quality in bearings, and Mr. Darby's remarks support the author's statement relative to lead content specifications.

There can be no question as to lead contamination from the tinning metal where solder is used. The author had this in mind as a distinct source of contamination and it is his understanding that on the higher lead tin-base babbitt (1 to 2 per cent.) the price differential is sufficiently great to warrant the use of pure tin for a tinning metal.

The author can see no reason for using solder (except for price consideration) as a tinning metal in connection with "lead-free" babbitt when contamination is known to occur. Not only does the lead contaminate the tin-base babbitt but in many instances the drosses become mixed and consequently the value of the babbitt dross is decreased. With pure tin, if the drosses become mixed, the value should be increased.

W. A. COWAN, Brooklyn, N. Y. (written discussion).—This paper presents interesting and valuable information relating to the utilization of secondary metals. Many practical suggestions are given.

The statement that the presence of antimony in tin-lead solder is undesirable is particularly true where the solder is to be used on metallic zinc or galvanized iron. However, the presence of antimony in solder to be used on other metals in amount no greater than 2 per cent. may not be detrimental and may even be of some advantage in respect to the qualities of fluidity and adhesion.

Statement is made that as much as 2 per cent. of lead would not be objectionable in most babbitt bearings. It has, in fact, been stated in a previous article¹ that the addition of 1 per cent. of lead to a tin-base babbitt metal of ordinary composition improves the hardness and antifrictional qualities. Diagrams were given in the article referred to showing the hardness of certain alloys of this kind at various temperatures. On the other hand, it has been reported that the addition of lead to these alloys tends to cause them to crack in service and also that it may lessen their strength at high temperature. It seems probable that, because of the somewhat greater hardness imparted by the addition of lead, at the same time there may be caused some decrease of toughness or increase of brittleness, thereby causing a greater tendency of cracking. There may be further reason for occurrences of cracking because of a characteristic of the structure of tin-base alloys containing a small percentage of lead, which was pointed out in an article by the writer,² presented by synopsis at the meeting of the British Institute of Metals in September, 1927. Here it is shown that in tin-base alloys of this kind minute cavities are found in the cast metal, when it contains some lead, due to the shrinkage of segregated portions of liquid eutectic having relatively low freezing point compared with that of the bulk of the alloy.

¹ J. L. Jones: Babbitt and Babbitted Bearings. *Trans.* (1919) **60**, 458.

² W. A. Cowan: Minute Shrinkage Cavities in Some Cast Alloys of Heterogeneous Structure. *Abs. in Engineering* (1927) **124**, 367 and *Metal Ind.* (1927) **25**, 488.

Metal Recovery from Bronze Foundry Slags

BY ERNEST R. DARBY,* TOLEDO, OHIO
(New York Meeting, February, 1928)

WHEN bronze is melted in open-flame furnaces a considerable amount of slag is formed during the melting operation. This slag may be incidental to the melting practice or it may be formed intentionally by slag-forming constituents added to the furnace charge to provide a covering for the melted metal.

When this slag is removed from the furnace, it contains, in addition to the free metal carried with it by the skimming operation, a considerable amount of metal as oxide either combined or mechanically mixed with it. By the usual crushing and washing methods this metallic oxide generally goes to the tailings pile, so diluted by other foundry waste that its recovery is economically impossible. If this furnace slag is not mixed with other foundry waste, practically all of the metal oxide as well as the free metal may be recovered by some form of smelting operation.

The first side of the problem to be considered is the amount of slag produced. It may not be true that the majority of foundries have no record of the amount of slag made, but it is certainly true that a very great many either have no record or pay little attention to it. Usually the collection of furnace slag for one normal week's run will be sufficient to determine the advisability of its being handled in a different manner from the crushing and concentrating generally employed. If a large representative sample of the accumulation is crushed and concentrated and the recovery compared with the results of a careful assay, it will be found that a large percentage of the total metal content was lost in the washing process. The percentage of loss will be greater than the metallic oxide content, as some free metal in extremely fine particles always is carried away in grains of slag. From such a comparison, it may be determined whether or not the slag should be melted, sold or treated as before. An example of an actual test of this kind is given below.

In a foundry melting 50,000 to 80,000 lb. of bronze per day, a week's accumulation of furnace slag and ladle skimings amounted to 16,500 lb.—over three times as much as the foundry superintendent estimated before the accumulation was made. Two tons of this material was taken as representative of the lot. This was ground through a thoroughly cleaned ball-mill and concentrated over a Wilfley table. The

* Metallurgist, Bunting Brass & Bronze Co.

metal taken from the mill and the concentrates from the table were melted together in two crucibles, using a flux of soda ash and charcoal. The fire assay of the original lot was made from a 2000-lb. sample crushed and quartered to 50 lb. The comparison of this with the result of the concentrating test is given in Table 1.

TABLE 1.—*Comparison of Concentrating Test with Fire Assay*

	Analysis				Extension			
	Copper, Per Cent.	Tin, Per Cent.	Lead, Per Cent.	Not Deter- mined, Per Cent.	Copper, Pounds	Tin, Pounds	Lead, Pounds	Not Deter- mined, Pounds
Total concentrates 682 lb....								
Ingot poured 576 lb.....	76.38	6.22	15.30	2.10	439.95	35.83	88.13	12.10
Crucible slag 122 lb.....	1.74	1.18	0.80		2.12	1.44	0.98	
Total recovery by concen- tration.....					442.07	37.27	89.11	12.10
Assay 28.5 per cent. 4000 lb. = 1140 lb.....	74.50	12.30	11.16	2.04	849.30	140.2	127.20	23.3
Recovery by concentration..					442.07	37.27	89.11	12.10
Difference.....					407.23	102.93	38.09	11.20

This comparison shows a loss by concentration of approximately 560 lb. of metal made up of 72.5 per cent. copper, 18.5 per cent. tin and 7.0 per cent. lead. It was calculated that the loss during one year would amount to about 115,000 lb. of metal, of which more than 20,000 lb. would be tin.

A blast furnace was installed to handle the furnace slag, and the recovery during the first two months was more than satisfactory. The slag smelted amounted to slightly over 140,000 lb. from which 41,300 lb. of metal were recovered. As before, 4000 lb. of the accumulation were crushed and concentrated, and from the results of this sample the saving effected by the blast furnace was computed. The figures are given in Table 2.

The saving at this particular plant in one year, after deducting the total cost of the furnace, was over \$13,000.

It is interesting to note that the 20,000 lb. of metal actually saved by the blast furnace shows a tin content of nearly 4000 lb., approximately 20 per cent., while the average tin content of the foundry product was only 6.25 per cent. This illustrates the effect of selective oxidation.

In another instance, 90,000 lb. of skimmings purchased from an outside source were charged in a reverberatory melting furnace from which approximately 53,000 lb. of metal and 37,000 lb. of slag were recovered. The slag was smelted in a blast furnace, and yielded nearly 6000 lb. of

DISCUSSION

G. H. CLAMER, Philadelphia, Pa. —Years ago we had smelters in our plant, and reached rather a different conclusion from that reached by Mr. Darby; in fact, almost diametrically opposite. It is entirely a matter of the quantity of material that must be handled as to whether you treat it by a wet process or by the smelting process. To put in a wet concentrating plant that is highly efficient, and one from which a large recovery may be obtained, costs a great deal of money. I think our installation ran up to about \$100,000. We found that, all things considered, it was best to concentrate in the wet way for the quantity that we had to handle and particularly because in putting it through the smelter there was a great deal of sulfur absorbed. It was necessary to greatly reduce the sulfur by reverberatory refining, in order to make the metal usable in the foundry.

If the smelting equipment is sufficiently large and efficient, it is probably economical to use the dry process. Every case must be handled on its own merits as to the cost of the equipment and the quantity available for smelting.

W. F. GRAHAM, Mansfield, Ohio. —Jotting down the figures of production and the amount of slag, it would seem that Mr. Darby's gross loss before recovery or treatment was approximately 6 per cent. I wonder if that was correct? Also, what was the copper content of the tailings, that is, the material discarded, and what was the percentage of recovery in brass value? In other words, would the difference between that and the gross loss be the net loss?

E. R. DARBY.—The figures I gave were partly from the paper and a great deal from memory. Percentages were given as round numbers. In one foundry of which I know, the total loss, that is net loss, as figured from the recovery from concentration, was in the neighborhood of 4 per cent.

The question as to the value of the operation, I can best answer in this way: In one plant producing considerably more than I was referring to here, the furnace installation cost in the neighborhood of \$5000. Thirty to forty pounds of slag per melting furnace was produced in the foundry. That slag was all accumulated and run at the end of the month. In the course of a year, a net profit of \$18,000 to \$20,000 was shown from the value of the material reclaimed, which would not have been reclaimed had the wet process been used.

W. F. GRAHAM.—What was the percentage of copper in the tailings?

E. R. DARBY.—The tailings showed about 0.75 per cent. copper by ordinary methods of analysis. I am not too sure that they were correct.

S. ROLLE, Carteret, N. J.—How about tin?

E. R. DARBY.—I do not think it was determined.

C. O. THIEME.—What was the composition of that particular bronze? Was it high in tin?

E. R. DARBY.—The tin in the bronze melted in that foundry averaged about 7 per cent. tin. The lead content was fairly high.

S. ROLLE.—You mentioned a 50 per cent. loss. What did that refer to?

E. R. DARBY.—I meant 50 per cent. of that recovered in the blast furnace. Taking the blast-furnace recovery as 100 per cent., they were losing just about half of it before.

G. H. CLAMER.—Eight or ten years ago we had presented before the Institute of Metals two papers on this subject.¹ The paper by Taggart was on concentrating

¹ A. F. Taggart: The Reclamation of Brass Ashes. *Trans. Amer. Inst. of Metals* (1916) 10, 66.

J. L. Jones: The Selling of Brass Foundry Refuse. *Trans. Amer. Brass Founders' Assn.* (1910) 4, 59; also *Metal Ind.* (1910) 8.

by the wet process, and the paper by Jones on the same subject as now discussed by Mr. Darby. Of course, in referring to those papers you must remember that they were written a number of years ago, and that the practice today is somewhat different. They were very interesting papers and you would do well to read them if you are interested in the subject.

E. R. DARBY.—In connection with this blast-furnace operation, I am simply offering that as one means of perhaps improving a method of reclaiming. Undoubtedly, there are many other means. The blast furnace is very suitable to most operations. Just because there is not enough slag or other material to keep the blast furnace going all the time does not mean that it will not pay. Two or three days' run at the end of the month will save money.

As Mr. Clamer has brought out, its fault is that the material recovered by means of a blast furnace contains percentages of sulfur and percentages of iron. They must be handled in two ways; they must be taken out, or the metal must be used in small amounts so that by dilution the impurities mean nothing in the foundry product. The blast furnace can be operated so that the minimum of sulfur and iron can be introduced into the metal. At the present time the plant I am with is operating a blast furnace with the sulfur content very low indeed and the iron content, as a rule, does not exceed 0.5 per cent., or 0.75 per cent. at most. If that material is particularly beneficial in some mixes, we refine it; if it is not, we use it for its tin content in very small quantities, so that when the melt is made in the foundry the impurities really amount to a negligible quantity in the product.

W. F. GRAHAM.—Mr. Darby's figures check our experience at the Ohio Brass Co. very closely with reference to open-fire furnaces but not necessarily with electric furnaces of either the induction or indirect arc types.

E. R. DARBY.—The paper has to do preferably with the open-flame furnace, which is the one found in the average bronze foundry. It applies to crucible melting with coke, also.

G. H. CLAMER.—Of course, the smelting of slag material—material that is in a semifused state—is much easier than to attempt to smelt something in the granular or powdered form. Finely divided material must be briquetted.

E. E. THUM, New York, N. Y.—Mr. Darby's paper reminds me of considerable discussion we had during war times about the proper way to reclaim zinc waste. Many suggestions were made as to how brass foundries could conserve resources most advantageously in those times of stress. Both that problem and this boils down to one of relative cost. Looking over the western metallurgical field—the place where the zinc, copper, and lead come from—we see a very pronounced tendency for the smaller treatment plants to close, and the smelting to be done in a few very large ones. That seems to indicate that an individual foundry would not find much profit in working up a few tons of its own waste. It is not easy to get a good recovery of any type of raw material, particularly, I would judge, if it is foundry slag. It requires not only good, well balanced equipment, but also well educated and resourceful men—specialists. These men are not found in foundry organizations. Consequently, it would seem to me that the most important thing, as the speaker pointed out, is to look very carefully into the cost of smelting foundry slag before undertaking it. It would seem almost certain that if there is a good smelting company near by, it would be better from the dollars and cents standpoint to sell the slag outright and forget about it, particularly if there is any competition for that particular kind of material. If the secondary smelter will not pay enough to warrant the collection and transportation of the wastes, it is a pretty safe bet that it is not going to pay a foundry organization to collect and smelt them.

Remelting Secondary Aluminum

BY T. D. STAY,* D. B. HOBBS* AND H. O. BURROWS,* CLEVELAND, OHIO

(New York Meeting, February, 1928)

ALUMINUM which has lost its original identity as to source may be considered as secondary. This would include scrap originating in the fabrication of aluminum, which is not consumed at the plant of fabrication, and all material resulting from fabrication, which has lost its original identity regardless of whether it be consumed at the plant of fabrication or not. In general, secondary aluminum may be divided into two classes, commercially pure and alloyed. The chief impurities found in commercially pure aluminum are copper, iron, titanium and silicon; while in aluminum alloys, copper, iron, titanium, silicon, zinc, manganese, magnesium, nickel, or tin, may be present in varying proportions. Occasionally lead and antimony are found in secondary aluminum alloys, especially if the alloy results from remelting vender's automotive scrap. Such alloyed elements as are found in the scrap cannot be removed on remelting. In this, the remelting of secondary aluminum differs from the smelting of secondary copper or most other secondary metals.

The majority of secondary materials reach the consumer in the form of remelt ingot or remelt No. 12 ingot. This ingot varies greatly in quality, depending upon the source of the material, and the manner in which it is refined and blended. The principal differences between primary and secondary ingot are:

1. The composition of secondary ingot may be more or less indefinite.
2. Secondary ingot may contain more dross and oxide.

Secondary ingot may, however, be used successfully in a great many products.

RELATION OF PRIMARY PRODUCTION TO SECONDARY PRODUCTION

Table 1, compiled from data published by *The American Metal Market*, gives an approximate idea of the relation of primary to secondary production. Information obtained from other sources leads the authors to believe that the figures for secondary production are somewhat low.

* Aluminum Co. of America.

TABLE 1.—*Relation of Primary Production to Secondary Production in the United States*According to Data Published by *The American Metal Market*

Year	Primary Production		Secondary Production		Total Production, Pounds
	Pounds ^a	Per Cent.	Pounds ^a	Per Cent.	
1913	64,900,000	87.5	9,308,000	12.5	74,208,000
1914	90,000,000	90.9	9,044,000	9.1	99,044,000
1915	99,000,000	85.3	17,000,000	14.7	116,000,000
1916	139,000,000	78.3	38,600,000	21.7	177,600,000
1917	200,000,000	86.1	32,200,000	13.9	232,200,000
1918	225,000,000	88.2	30,100,000	11.8	255,100,000
1919	198,000,000	84.1	37,382,000	15.9	235,382,000
1920	198,000,000	86.5	31,000,000	13.5	229,000,000
1921	63,388,000	78.0	17,800,000	22.0	81,188,000
1922	114,640,000	77.9	32,580,000	22.1	147,220,000
1923	213,820,000	83.4	42,600,000	16.6	256,420,000
1924	187,392,000	77.6	54,000,000	22.4	241,392,000
1925	205,030,000	70.0	88,000,000	30.0	293,030,000

^a *Metal Statistics* (1927).

TYPES AND SOURCE OF SECONDARY METAL

Clip and Sheet.—Scrap of this nature may be divided into commercially pure and alloyed clip and sheet. Under each of these divisions, the material may be subdivided into clean and dirty. The gage of the material is also of importance. Clip and sheet scrap may be either loose or baled. Cooking utensil plants, automobile body works, and other users of aluminum sheet, usually dispose of this material on the open market. It is from such sources that secondary aluminum clip and sheet are derived. This material has always been considered the best scrap on the market, and has always brought the highest prices. Commercially pure aluminum clip and sheet may be used to make high grade remelt ingot. It may also be used directly in making castings. The authors do not consider it good practice to make castings direct from exceedingly dirty and thin material. Such material as this should be remelted first to remove non-metallic impurities.

Foil.—Foil is sheet, about 0.0002 to 0.0005 in. thick, made from commercially pure aluminum. It may be either clean or contaminated with paraffin, shellac, paper, paint, or various other material. Because of its extreme thinness, it can not be remelted in the same manner as clip and sheet. If properly handled, foil scrap may be recovered in a good grade of remelt ingot.

Cable.—Aluminum cable consists of commercially pure aluminum which has been drawn into wire and stranded into cable. It may be all

aluminum or steel-reinforced, either bare or insulated. "Clean" cable consists only of all aluminum cable, not corroded; while "dirty" cable consists of all other cable. About the only source of supply is that of discarded cable from power transmission lines.

Castings.—Aluminum, either commercially pure or alloyed, which has been cast in either sand, die, or permanent molds, and has been discarded, constitutes casting scrap. Foundry defectives, gates and risers, cannot be classed as secondary casting scrap, as these are charged directly into subsequent heats made in the foundry where this scrap originates. Very few foundries dispose of their scrap castings on the open market. As a rule, casting scrap is accumulated in small quantities by dealers in secondary metals who have salvaged automotive parts and other discarded castings.

Scrap castings may be classed as follows:

1. Clean casting scrap. This type of casting scrap includes new rough castings which have for some reason or other become obsolete, or castings from machine shops which have not been assembled in motors or used to the extent of becoming covered with grease or dirt. They may, however, be coated with oil that might have gotten on the castings during machining operations.

2. Dirty casting scrap. Such scrap castings as those which have seen service in motor cars and the like may be considered under this classification. These castings are usually covered with a considerable amount of grease and dirt. Nuts, bolts, brass bushings, etc., are usually associated with casting scrap of this nature.

3. Dirty casting scrap, cleaned. This type of casting scrap includes such castings from the second classification from which practically all oil and grease and loose iron, brass, etc., have been removed.

The limit to which each kind of casting scrap may be used depends upon the thoroughness with which it is graded. Casting scrap is used primarily in the production of what is commonly known as remelt No. 12 ingot.

Borings, Turnings and Sawings.—The by-product from machining operations may be considered under this classification. As a general thing, this grade of material is alloyed. It will vary in the amounts of foreign material from 1 to as high as 50 per cent., depending upon the care taken in the machine shop to keep the borings free from floor sweepings, iron and steel borings, brass, babbitt, oil, machining compounds, dirt, and moisture. Any shop machining aluminum is a potential source of borings, turnings and sawings. Manufacturers of automobiles and automotive equipment offer the largest source of supply. From a recent investigation by the authors, it was found that approximately 10 to 12 per cent. of the rough weight of aluminum castings made for automotive consumption is removed by machining operations. This 10 to 12 per cent.

machined from the castings is returned to remelting plants for recovery. It is generally considered uneconomical to charge this grade of material into heats as such, without first refining, pigging and analyzing. The analyzed ingot, thus obtained, is suitable for making remelt No. 12 ingot.

Skimmings.—Skimmings result from any melting operation, and are a mixture of oxides and aluminum with foreign matter. In remelting aluminum, material collects on the surface of the bath. This material is in the form of an emulsion, and is removed from the surface of the bath by skimming. Skimmings may be either commercially pure or alloyed, depending on the metal from which they are removed. This grade of material will vary in the amount of metallic content, depending on the type of metal melted, the type of furnace in which it is melted, the furnace atmosphere, and the efficiency of the operation. Some plants recover their own skimmings, while others sell them on the open market. As in the case of borings, it is better not to use this grade of material until it has been refined. The ingot obtained from this material is suitable for making remelt No. 12 ingot.

Grindings and Buffings.—This grade of material is the refuse from cleaning and polishing operations. The fineness of grindings and buffings, as well as the amount of non-metallic impurities in them, depends upon the type of the grinding and polishing medium. The material can be used only after it has been refined, pigged and analyzed.

Sludge.—Sludge is the residue found at the bottom of the bath during the refining of certain types of material. It is usually a conglomeration of bolts, nuts, pipes, wire and other articles, mixed with aluminum. Aluminum can be removed from this mass with difficulty, and because of this, the greater part of this material is considered worthless.

Dross.—This is the residue resulting from a fluxing operation. Dross is chiefly aluminum oxide, but may contain aluminum nitride, and aluminum carbide as well as an appreciable amount of metallic aluminum. Any other elements present in the bath may also be present in the dross in the form of oxides, nitrides and carbides. The bulk of the metallics may be removed from this material by mechanical means, and remelted into ingot form. The ingot if properly handled is suitable for making aluminum alloys for foundry use.

RELATION OF MARKET PRICES—PRIMARY TO SECONDARY

The relation of the market price of primary and secondary aluminum depends to a great extent upon the amounts of primary and secondary materials available and the demand for each. This relation is shown in Fig. 1.

The market prices referred to in various daily metal trade papers for aluminum clip, scrap castings and borings are the prices dealers in secondary materials are willing to pay for ordinary scrap in comparatively

small quantities, and do not represent the prices paid for this grade of material by consumers who use it in large quantities. As a rule, this material, as purchased by the average dealer in secondary material, is in

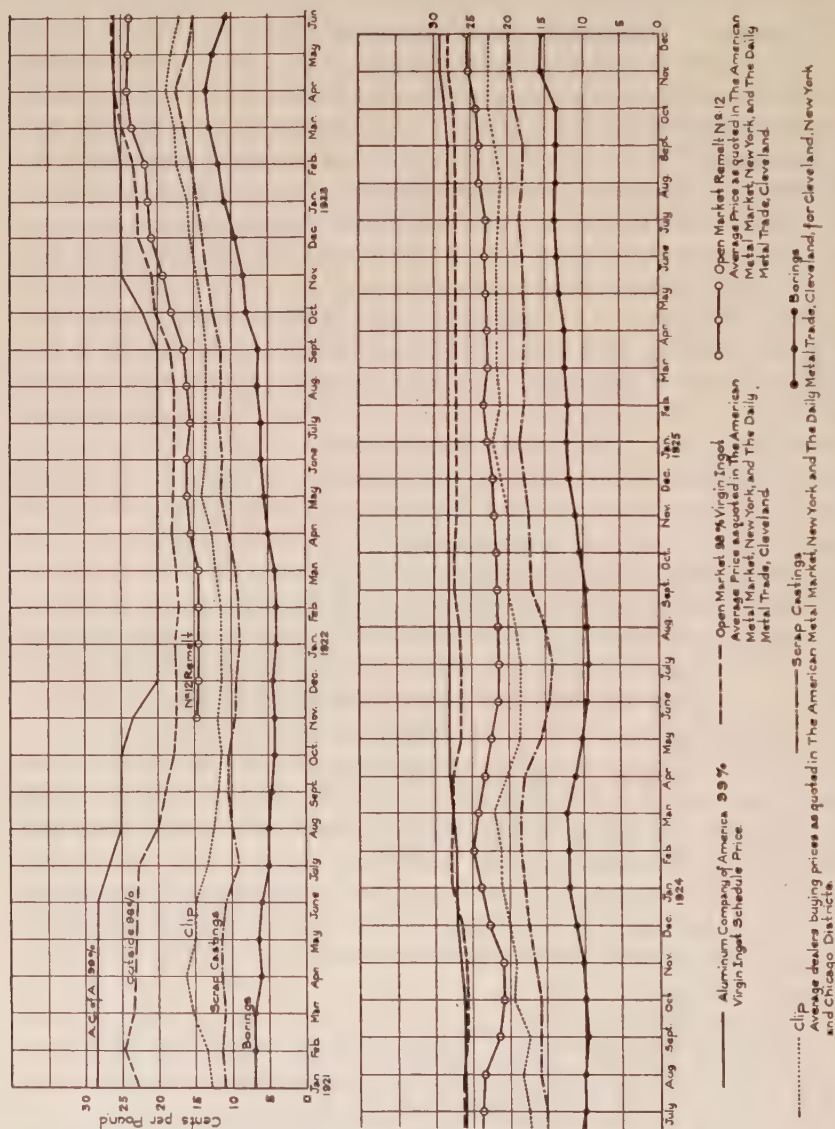


FIG. 1.—RELATION OF MARKET PRICES, PRIMARY TO SECONDARY ALUMINUM.

small quantities, and is contaminated with oil, dirt, moisture and other foreign material. These dealers in some cases remove part of this foreign material and sort the scrap. This scrap may pass through several dealers' hands, each collecting his revenue before it is accumulated in carload lots.

According to a private communication received by the authors from one of the metal trade papers, dealers' buying prices, as appearing in the trade papers, are based on a canvas of the dealers in the various market centers. These prices are naturally lower than the prices ultimate consumers pay for larger lots of carefully sorted and cleaned material.

UNDERLYING PRINCIPLES RELATING TO REMELTING SECONDARY ALUMINUM

Theory of Melting.—All aluminum is coated with a layer of oxide, possibly mixed with nitride or carbide. This covering is heavier on old material than it is on new material. When ingots, scrap castings, and other forms of heavy material, are charged into a furnace to be melted, without the aid of a molten heel, melting starts within the solid material. Molten metal breaks through the oxide film on the surface of the solids, and forms globules. Each of these globules, coated instantaneously with a new film of oxide, drops to the bottom of the container. The oxide casings are broken by the fall, and coalescence easily takes place.

The surface of the molten metal gradually rises around the melting solids. As the particles of molten metal are freed from their surrounding films of oxide and coalesce, their oxide casings rise to the surface of the molten metal where they are trapped by the oxide skin formed on the surface. Any solid metal, which melts underneath the surface of the molten metal, coalesces with the liquid immediately, since in the absence of oxygen no oxide coating can be formed. But if globules melt away from the solid metal above the surface of the molten metal, they must not only break their enveloping films, but also that of the surface of the molten metal before coalescence can take place. Each time a film of oxide is broken and molten metal is exposed to the air, a new oxide film forms immediately; consequently metal melting above the surface of the liquid is constantly increasing the oxidized material.

As the pieces of solid metal melt out of their original enveloping shells, the oxide coverings become weak, and fall or rise to the surface of the molten metal. Thus on the surface of the completely molten metal is a layer of oxide under which there are other layers and particles of oxide intermixed with molten aluminum. "This might be pictured as a honeycomblike formation with the trapped particles of molten aluminum as the honey and the film of oxide as the comb. In other words, there is an emulsion of a solid (the film) and a liquid (the metal). If this emulsion is not entirely broken up and the metal freed from the enveloping film, the whole mass of oxide with the trapped metal will be skimmed off from what metal has coalesced."¹

¹ H. W. Gillett and G. M. James: Melting Aluminum Chips. *Bur. Mines Bull.* 108 (1916).

Borings, sawings, turnings and other small pieces of aluminum, melted without a molten heel, form coatings, as do the globules formed in the melting of ingots and other larger pieces of aluminum. The size of the molten borings, sawings, and other related material is smaller, and unless the weight of the particle melted is sufficient to cause the molten metal within to break through its enveloping film, little or no coalescence will take place. By puddling this mass of small particles, each enveloped in a covering of oxide, the films can be broken and partial coalescence effected.

In order to separate the molten aluminum from the layers of oxide at the surface, some suitable flux should be employed. The flux should be of such a nature that it will not permit molten aluminum to wet the oxide. The oxide after fluxing can be considered as dross, and can be readily removed from the surface without removing appreciable amounts of molten aluminum.

From the foregoing theory of melting, it is apparent that less oxide is formed when the material being melted is completely surrounded by molten metal. Therefore, it is logical to submerge as much of the material as possible in a molten heel. Where various grades of material are being melted, and no molten heel is available, those that oxidize the least should be melted first, and the other ingredients of the mix should be charged and immediately submerged after the molten heel has been obtained. In the case of borings, it is good practice to remelt some ingot previously made from borings, and charge the borings into this molten metal. After charging the borings into the molten metal, they should be stirred under the mass and puddled. In all cases the temperature of the metal should be kept as near the melting point as is consistent with operating conditions.

Sperry² states: "The best way to melt aluminum scrap, such as sheet or chips, is to have a pot of molten aluminum at low red heat and then to add the scrap to it, pushing it down at once under the surface, so that it is not exposed to the air at all. In this manner there is no oxidation of the aluminum and it can be melted with the minimum waste. The scrap will dissolve in the molten aluminum, and this is an ideal condition." He also states;³ "The chips should be added in small quantities at a time to already molten metal with immediate stirring, and the pot fluxed at the end of the melt with a little zinc chloride."

Vickers⁴ suggests practically the same method. Another description⁵ of this general method follows:

² E. S. Sperry: Questions and Answers. *Brass World* (1913) **9**, 296.

³ E. S. Sperry: Making Aluminum Ingots from Chips or Borings. *Brass World* (1910) **6**, 278; *Jnl. Inst. Metals* (1911) **5**, 342.

⁴ How to Melt Aluminum Turnings or Borings. (Editorial) *Foundry* (1913) **41**, 119.

⁵ Recovery of Aluminum Turnings and Borings—Problems of the Brass Founder. (Editorial) *Foundry* (1915) **43**, 195.

"The melting of finely divided metal entails considerable work, and furthermore, the material must be handled in a manner which will prevent undue oxidation. The best way to accomplish this is to dissolve the finer metal in a bath of molten metal. A large crucible should be used and the molten metal should be obtained by melting ingots or other bulky stock. In the case of aluminum, the bath should be raised to a temperature not above red heat. Charge as many borings at a time as the bath will dissolve, but do not leave any of the borings on top of the bath in a solid state. These should be stirred into the molten metal. Inasmuch as the bath increases with each charge of borings, it will dissolve more each time that additions are made. As the borings will cool the bath, the furnace should be closed from time to time, the metal again heated to redness, when more borings can be added, and this process can be continued alternately until the pot is full. At this stage the metal is cast into ingots, but sufficient should be left in the pot to form another bath. If the mushlike dross gathers on the surface of the metal, add a small piece of fused zinc chloride and stir it on the surface. This will liberate the metal from the dross, which will form a cover for the aluminum. The metal should be skimmed before casting into ingots. Incidentally, this dross is of no value."

Echevarri,⁶ Coulson⁷ and others also advance similar methods for remelting secondary aluminum.

FLUXES

A flux is any material which accelerates a separation of the metallic globules of aluminum from the enveloping films of oxide, nitride, etc. Fluxes for aluminum may be divided into three classes, namely: (1) those used principally as liquid covers, such as sodium chloride, in order to reduce oxidation losses and effect a slight solution of aluminum oxide; (2) those that actually dissolve the aluminum oxide, and thus induce coalescence of the fine particles, such as alkali double fluorides, and (3) those that are volatile at normal remelting temperatures, and are useful because of their thermal and mechanical effects, such as zinc chloride.

The properties of specific fluxes have been discussed at length by Gillett and James⁸ and by others. There are innumerable fluxes on the market for which various claims are made. In the opinion of the authors, an ideal flux should meet the following requirements:

⁶ J. T. W. Echevarri: Aluminium and Some of Its Uses. *Jnl. Inst. Metals* (1909) **1**, 125.

⁷ J. Coulson: Reclamation of Magnalium from Turnings. *Trans. Am. Inst. Metals* (1915) **9**, 336-342.

⁸ H. W. Gillett and G. M. James: *Op. cit.*

1. It should have the power to reduce the effective surface tension of globular aluminum particles. When the surface tension of the globules has been reduced, coalescence will take place more easily.

2. It should have the power to dissolve or absorb aluminum oxide. In dissolving or absorbing the aluminum oxide coating, which separates the globules, coalescence can be effected more readily.

3. It should be inexpensive.

4. It should react at a low temperature.

5. It should not appreciably attack the container. All fluxes will to an extent attack the container, and with some fluxes this is quite an item.

6. It should not appreciably affect the composition of the material being treated.

7. It should be nondeliquescent.

8. It should have a density less than that of aluminum.

9. It should be nonpoisonous.

EVALUATION OF SECONDARY ALUMINUM

Secondary aluminum is often contaminated with foreign material. This foreign material may be either metallic or non-metallic. Free iron in the form of nuts, bolts, pipes, borings, turnings, etc., and babbitt metal bushings, either attached to crank cases and other automotive parts, or present in borings, turnings, etc., make up the bulk of the metallic foreign material. Grease, oil, dirt, paper, moisture and aluminum oxide, constitute the majority of the non-metallic materials associated with secondary aluminum. In case the metallic foreign materials associated with the secondary material are present in appreciable quantities, they must be removed before remelting takes place, or they will alloy with the aluminum and materially alter the composition of it. The non-metallic impurities either volatilize or are skimmed off on remelting. The metallic recovery from any lot of secondary aluminum is, therefore, to a great extent dependent on the percentage of foreign metallic and non-metallic material associated with it. The fineness of the secondary aluminum also bears a relation to the recovery.

Assay.—In order to determine approximately what recovery may be expected from any lot of material an assay should be made. This is especially true in the case of borings, skimmings and other fine material, as well as thin gage sheet, foil and extremely dirty material. Two forms of assay commonly in use are the laboratory and shop assays. The character of the material determines which method of assay should be employed. The laboratory assay gives a slightly higher recovery; while the shop assay more nearly approaches the actual working conditions and gives a recovery nearer to that obtainable in practice.

Laboratory Assay.—In making a laboratory assay for borings, turnings, sawings, buffings, and grindings, the following physical and chemical characteristics should be determined: (1) percentage of oil and moisture; (2) percentage of free iron; (3) metallic recovery, and (4) chemical analysis of recovered metal.

The sampling should be done in such a manner that it will be representative of the entire lot. This is best accomplished by taking a small quantity from various locations throughout the entire lot, and mixing these samples thoroughly. Aliquot portions should be taken until a sample of approximately 1 to 2 lb. is obtained. From this sample, 200 gm. are taken, spread on a watch glass, and dried in an oven for 1 hr. at 105° C. (221° F.) in order to expel the moisture. After cooling the sample in a desiccator it is reweighed, and the percentage of moisture calculated.

The dried sample remaining after the moisture has been expelled is thoroughly washed with gasoline in order to remove the oil. It is again dried and weighed. The percentage of oil present can then be calculated. The weighed sample, remaining after the free iron has been removed, is placed in a small graphite crucible in a muffle type electric furnace and heated to 704° C. (1300° F.). The crucible is then removed from the furnace, and 6 gm. of zinc chloride stirred into the molten metal until finely divided dross rises to the surface. The molten metal is poured from beneath the dross leaving only the dross in the crucible. Three grams of zinc chloride are added to the dross in the crucible and stirred in. The crucible is emptied and the contents allowed to cool. The dross is screened through a 20-mesh screen, and the metallic globules of aluminum remaining on the screen retained. The total aluminum recovered is weighed, and the percentage recovery determined. The recovered aluminum is then analyzed.

Shop Assay.—The metallic content of skimmings, sweepings, drosses and similar materials, vary appreciably within different sections of the same lot of material. For this reason it is extremely hard to secure a representative sample, and such types of material should be purchased on a metallic recovery basis rather than on the results obtained from a laboratory assay. If, however, the material cannot be purchased on this basis as large a sample as possible should be obtained for a shop assay. If the material is crumbly it should be crushed in a pulverizer to loosen the dust from the aluminum particles, and then passed over a 20-mesh screen. The material which does not pass through the screen is remelted in the manner described under the pot method of remelting skimmings later on in this article. Having the original weight of the material and the weight of the metal recovered, the percentage recovery can be obtained. From the recovered metal a chemical analysis is made.

REMELTING EQUIPMENT AND PREPARATION OF SECONDARY ALUMINUM
FOR REMELTING

Clip and Sheet.—Clip and sheet require no special preparation for remelting, unless it is desired to bale it for convenience in handling.

Foil.—Clean foil may be briquetted and charged like heavy clip yielding high metal recovery. Such foil as is interleaved with paper presents another problem. The paper must be removed before the foil can be remelted. This may be accomplished by burning the paper off over a grating with a limited supply of air. The burning must be done very slowly or the foil will be badly oxidized and a very low recovery will result.

Castings.—Secondary aluminum castings are used almost exclusively in the production of alloys for sand foundries. Before this grade of scrap can be used, it should be cleaned of as much of the foreign material as possible. This foreign material may consist of sand, grease, iron, babbitt, brass bushings, etc. The metallic foreign matter, such as nuts, bolts, pipes, bearings, etc., may be either removed by hand or by liquating; while the non-metallic contaminations, oil, grease, dirt, etc., may be either scraped off or burned off. Scrap castings are often in large pieces which cannot be charged into small pots, and unless a reverberatory furnace is employed, they must be broken up.

Borings.—Aluminum borings contain varying percentages of foreign matter such as dirt, iron and steel chips, cutting compounds, etc. The percentage of metallic and non-metallic foreign matter, associated with the aluminum borings, will vary from a fraction of a per cent. in some cases to as high as 60 to 80 per cent. in others.

The cutting compound with which aluminum borings are soaked is, as a rule, either an oil-base or a water-soluble alkaline base compound. If the compound is a water-soluble alkaline base compound, the borings are very apt to disintegrate if allowed to remain in storage for any length of time. For this reason, the compound should be removed in a comparatively short time. Oil-base compounds do not cause the borings to disintegrate, and borings soaked in such compounds may be stored for indefinite periods before remelting. As a rule, however, the longer the borings stand before refining the lower the recovery will be. The most common methods for removing the cutting compound are in either a centrifugal or rotary steel drier.

If more than 1 or 2 per cent. of metallic or free iron is present, it should be removed before the borings are remelted. This is best done by passing the borings through a magnetic separator after they have been dried of the cutting compounds. Machine shops have been made to see the advantage of exercising great care in segregating aluminum borings from other foreign matter, consequently, a better grade of aluminum

machine scrap results, and in a great many instances it is not necessary to pass them through a magnetic separator.

Some plants briquette the borings before charging them into furnaces for remelting. Much has been said pro and con by Sperry,⁹ Hirsch,¹⁰ Gillett,¹¹ Gillett and James,¹² and others. The chief claim for briquetting borings is that sufficiently high recovery is obtained to more than offset the cost of briquetting. The authors, however, after a careful investigation have been unable to bear out this statement. The results in Table 2 show that in this test no advantages have been gained from briquetting borings.

TABLE 2.—*Comparison of Operating Efficiencies, Briquetted and Loose Borings from the Same Lot of Material*

Figures for Loose Borings Arbitrarily Taken as 100 and Ratios Calculated for Briquetted Borings

	Ratio of Briquetted Borings to Loose Borings Mechanically Puddled in Iron Pots
Recovery.....	93.7 to 100
Charge rate per furnace hour.....	81.8 to 100
Charge rate per man hour, direct labor.....	79.2 to 100
Ingot produced per man hour, direct labor.....	106.6 to 100
Ingot produced per furnace hour.....	106.9 to 100
Ingot produced per gal. fuel oil.....	94.7 to 100
Ingot produced per lb. flux.....	99.3 to 100
Production costs.....	139.7 to 100

Skimmings and Dross.—This material varies in aluminum content from only a few per cent. in some drosses to as high as 95 per cent. in "skimballs." If the skimmings are crumbly, and contain a large percentage of fine dust and oxide, it is advantageous to remove the fine material before remelting. This may be accomplished by crushing the material in a suitable hammer mill. The action of this mill is not so much to crush the skimmings as to jar loose the fine dust. The fine particles may then be removed by passing the crushed material over a 20-mesh vibrating screen. The fine material which passes through is practically free from recoverable material, and is discarded. That which does not pass through the screen is ready for remelting. Before charging it into the furnace, however, the operator should remove the free iron.

⁹ E. S. Sperry: The "Ronay" Process of Briquetting Metal Chips. *Brass World* (1911) 7, 41.

¹⁰ E. F. Hirsch: Metallbriketts. *Elektrotech. Zeitschr.* (1914) 35, 1092.

¹¹ H. W. Gillett: Melting Aluminum Chips. *Trans. Am. Inst. Metals* (1915), 9, 205-210.

¹² H. W. Gillett and G. M. James: *Op. cit.*

METHODS AND COST OF RECOVERY

Clip and Sheet.—Clean clip and sheet require no special remelting process. It may be charged directly into the furnaces; however, it is best to charge this grade of material after a molten heel has been obtained and submerge it immediately. In so doing, the chances for oxidation are minimized. Dirty clip and sheet should be remelted by puddling into a molten heel and fluxing.

Foil.—Clean foil may be successfully remelted in an iron pot furnace provided extreme care is exercised over the temperature of the molten heel at all times. The success of this operation depends upon keeping the heel pasty, and stirring the foil into this pasty mass. The only time the temperature should be allowed to rise much above the melting point of aluminum is during the fluxing operation. The temperature of the bath should be lowered before charging more foil. Foil from which the paper interleaves have been burned still contains charred paper. This foil may be remelted in the same manner as described for clean foil, but with slightly lower recoveries. It is difficult to remelt foil in a reverberatory furnace because of its tendency to float on the bath. Clean foil, which has been briquetted, may be remelted with very little oxidation by puddling into a molten heel.

Cable.—As previously stated aluminum cable is either all aluminum, or steel-reinforced, and may be either bare or insulated. Pure aluminum cable presents no remelting problems, and may be used directly in making castings in place of ingot, unless too highly oxidized.

In the case of steel-reinforced cable, the aluminum strands should be separated from the steel wire core before remelting. This type of cable may be cut into lengths of 6 or 8 in. by means of a power shear. The pieces of steel wire are separated from the aluminum strands by a magnetic separator. The pieces of aluminum wire may then be used directly in making high grade remelt ingot. Another method of melting this type of cable is that of melting the aluminum away from the steel wire as the cable is drawn through or over a bath of molten aluminum in a reverberatory furnace. This method is wasteful, however, as much of the aluminum sticks to the steel wire and is lost.

Insulated cable may be used direct in small amounts in making alloys in a reverberatory furnace; however, the burning insulation causes much smoke and dirt. It is better to remove the insulation first. This may be done by stacking the cable in piles and igniting it. The insulation is burned away, and the metal is left, usually mixed with burned material. It may be remelted, fluxed, and cast into remelt ingot.

The chief difficulty encountered in remelting cable is its unwieldiness. Scrap cable is usually shipped in coils of 3 or 4 ft., dia. which weigh approximately 100 lb. If a reverberatory furnace with sufficiently wide

door openings is used for remelting, the coils can be charged readily without trouble. If a furnace of this type is not available, it is better to cut the coils in half.

Castings.—Scrap castings present no remelting problems provided they have been cleaned or are clean. They should, however, be submerged in a molten heel on remelting to prevent excessive oxidation. In melting dirty castings, the use of a flux may result in a higher recovery.

Borings.—Aluminum borings may be remelted in both iron pots and reverberatory furnaces, either by hand or mechanical puddling processes. The various steps carried out in a plant for refining borings are shown in Fig. 2.

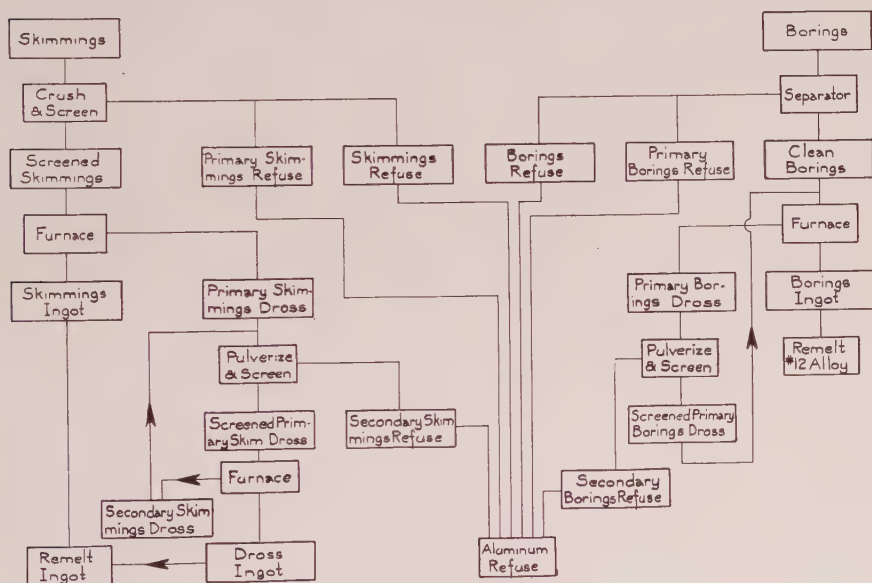


FIG. 2.—FLOW SHEET OF BORINGS AND SKIMMINGS RECOVERY PLANT.

Hand Puddled.—Puddling by hand is probably the oldest method used for recovering borings. The furnace may consist of an iron pot in a steel shell lined with fire brick. Either natural gas or fuel oil may be used. If a 300-lb. furnace is used, a molten heel of 80 to 100 lb. should be obtained by remelting boring ingot. Borings may then be added very slowly to this heel and stirred into it with an iron bar. This practice should be continued until the pot is nearly full when some suitable flux, such as zinc chloride, or a combination of zinc chloride and cryolite, is added. The charge should be only partially pigged and the operation started over. This process is not only slow, but tedious and back-breaking. The recovery obtained from hand-puddled borings depends upon not only the skill of the operator but also the vigor with which he works

the mass. Even the most skilled operators become fatigued before an 8-hr. shift has elapsed, and the recovery drops.

Mechanically Puddled.—Where production warrants, mechanical puddling methods should be employed. Depending upon the amount of borings to be recovered, either an iron pot or reverberatory furnace with mechanical puddling equipment may be used. Mechanical puddling is more satisfactory than hand puddling in that it, to a great extent, removes the human fatigue element. That type of puddler which mixes the borings into the molten heel most readily and uniformly has been found to give the best results. Different types of mechanical puddlers may be advisable for different types of material being handled and for different types of furnaces employed for remelting. In general though, it may be said that any mechanical puddler which will successfully handle borings will handle sawings and similar materials, and that any mechanical puddler which will handle skimmings will also handle drosses. A puddler which gives the best results on iron pot furnaces is also apt to give the best results on reverberatory furnaces.

Salt Process.—In this process, a quantity of salt is melted, preferably in a reverberatory furnace. Thoroughly dry borings are then charged, and puddled by hand into this bath, the object being to submerge the borings as quickly as possible. This tends to reduce oxidation to a minimum, thus increasing final recovery.

It was found in a thorough test of this method that the increase in recovery was only 0.4 per cent. over mechanical puddling. In this test, the slight increase in recovery was offset by greater production costs. The charge rate was reduced to about one-third, and the fuel costs increased. This method was found by the authors to be severe on the furnace lining, and the ascending acid fumes corroded the iron in the building and equipment.

Skimmings.—Aluminum skimmings may be remelted in either iron pots or reverberatory furnaces. The routing of skimmings through a remelting plant is shown in Fig. 2. It is essential that the skimmings be charged into the furnace as free as possible from iron, dirt and aluminum oxide. Such impurities materially affect the recovery and cost, and where possible these should be mechanically removed before remelting.

Pot Method.—In pot melting, a stationary iron pot furnace may be used. As a rule, these furnaces are fired with either natural gas or fuel oil. The authors do not feel that the size of the pot is of much importance as they have found that the slightly higher percentage recovery obtained in a pot of 300-lb. capacity is offset by a higher hourly charge rate for a pot of 900-lb. capacity.

It is best to charge the mechanically cleaned skimmings into a heel of molten metal. This heel is usually about one-third of the capacity of the pot. The size of the initial charge of skimmings should be sufficient to

make the whole mass pasty, yet small enough to be easily stirred into the heel. After a pasty condition is obtained, the charging and puddling is continued at a rate which will just keep the mass pasty. When the pot is half full, a small amount of flux should be added, then the entire pot charged full of skimmings, and allowed to heat without stirring. The flux added at this time aids in liquefying the charge in the bottom of the pot.

After the charge is thoroughly heated, the stirring should be resumed until the whole mass becomes uniformly heated, and the lumps broken up. This is best done by means of a hook-shaped flat bar, driving the hook to the bottom of the mass and turning the hot skim over the colder skim on top. The charge now consists of a bottom of molten metal with the oxide and dirt on top, and presents the appearance of red hot sand with globules of metal showing through it. The charge is now ready to flux.

Any suitable flux may be used. A small amount of mixture consisting of 85 per cent. cryolite and 15 per cent. zinc chloride, sprinkled over the surface of the red hot skimmings and stirred in, has been found to give satisfactory results. On continuing the stirring, the dross will begin to glow, and eventually become intensely white hot. Here it shows a tendency to ball up. The stirring is continued in order to break up the balls of dross, and to cool the whole mass to a bright orange color. By this time, any remaining balls of dross break up easily when rapped, and the mass has a powdery appearance. It can now be skimmed off with a perforated skimmer, care being taken to rap each skimmerful on the edge of the pot to remove any remaining metal. The dross is allowed to slide down an inclined, vibrated, corrugated cast iron plate to cool it, and spread at the bottom to permit thorough cooling. The metal remaining in the pot is partially pigged, and the operation started over.

Reverberatory Method.—For reverberatory remelting of skimmings, a natural gas or fuel oil-fired reverberatory furnace may be used, with the hearth, or bath, divided into two parts. One side of this hearth is entirely enclosed, and heated by direct flame from the burners. The other side is open, and is used as the working side. Connection between the two sides is maintained by low arched passages through the dividing wall below the surface of the molten metal. A heel of approximately half the capacity of the furnace is melted down, and flows out through the arches into the open or working side of the furnace to the same level as that inside in the heating chamber. The skimmings are then charged on top of the molten metal in the outside compartment and stirred into the heel with iron stirring bars. When the skimmings have become red hot a small amount of flux is added on top of the skimmings and stirred in. By stirring after adding the flux the whole mass of skimmings will be brought up to a white heat and will lump up. These lumps should be broken up and the stirring continued until the white heat has substantially disappeared. The dross will then be skimmed off with a perforated

ladle and passed over an inclined corrugated iron plate to cool. The cooled dross is then screened and crushed to separate mechanically as much as possible of the remaining metallic shot from the non-metallic dross.

The chief precaution to observe in remelting skimmings in either iron pots or reverberatory furnaces is that the addition of flux be carefully controlled so that no fluxing action takes place until as much metal as possible has first been worked out of the skimmings by hand puddling.

Grindings.—In remelting grindings, the chief factor in successful operation is close temperature control. The lowest temperature at which the grindings will melt should always be maintained. For this reason, it has been found best to use an iron pot of about 300-lb. capacity. As in the case of borings, a molten heel is added to the iron pot, and the grindings stirred in with an iron stirring bar. As soon as the grindings are at a red heat a small amount of flux is added, and the mass brought up to a white heat by continued stirring. The resulting dross is stirred until as much as possible of the aluminum particles is worked out. It is then skimmed off with a perforated skimmer and cooled. The furnace is partially pigged and the operation started over.

Buffings.—Buffings may be run in exactly the same way as grindings, when they are clean enough, and contain enough metal to permit this method of handling. A little should be charged at a time, and should be worked in thoroughly before continuing the charge. Buffings will not show a very good charge rate or percentage recovery as there is very little aluminum in them, and the aluminum which is present is very finely divided.

Manufacture of Sterling Silver and Some of Its Physical Properties

BY ROBERT H. LEACH* AND C. H. CHATFIELD,† BRIDGEPORT, CONN.

(New York Meeting, February, 1928)

THIS paper gives a brief summary of the process of manufacture of sterling silver, and some of its more important physical properties, as observed in commercial production of rolled sheet and wire. Although papers have been published by Turner and Smith,¹ Rose,² Sperry³ and Jordan,⁴ there are few technical data available, and unfortunately the time allowed for the preparation of this paper has not been sufficient to make it as comprehensive as the title might indicate.

ANALYSIS OF STERLING SILVER

Fine or pure silver is too soft for coinage and the manufacture of articles in which strength and resistance to wear are desired. From the earliest times of which we have record, copper has been the metal generally used to harden silver. Analyses of coins and silver articles from ancient tombs show varying amounts of copper, and old Roman silver objects in the British Museum have approximately the same analysis as our sterling. The first authentic record of the establishment of a standard alloy is during the reign of Henry II in England. During the twelfth and thirteenth centuries, the people in the Eastern Provinces of Germany had a reputation for the standard and purity of their silver coinage, and it is said that Henry II employed some of these Easterlings, as they were called, to improve and standardize the English coinage, which had become debased. The peculiar standard adopted is probably accounted for by the system of weights used. A troy pound contains

* Manager of Development and Research, Handy & Harman.

† Research Metallurgist, Handy & Harman.

¹ E. A. Smith and H. Turner: The Properties of Standard or Sterling Silver, with Notes on Its Manufacture. *Jnl. Inst. Metals* (1919) **22**, 149.

² T. Kirke Rose: On Annealing of Coinage Alloys. *Jnl. Inst. Metals* (1912) **8**, 86.

³ E. S. Sperry: The Manufacture of Rolled Sterling Silver. *Jnl. Franklin Inst.* (1907) **163**, 109.

⁴ L. Jordan, L. H. Grenell and H. K. Herschman: The Tarnish Resistance and Some Physical Properties of Silver Alloys. *Proc. Inst. Metals Div., A. I. M. E.* (1927) 460.

240 pennyweights, and the standard adopted was 11 oz. 2 pwt. of fine silver and 18 pwt. of alloy, the word "alloy" being used to designate the base metal.

Silversmiths adopted this same standard for their silver plate and have continued to use it ever since; the name "sterling" evidently being a contraction of "Easterling Alloy" as the standard alloy was called. Expressed in percentage, the silver is 92.5 and copper or other base metals

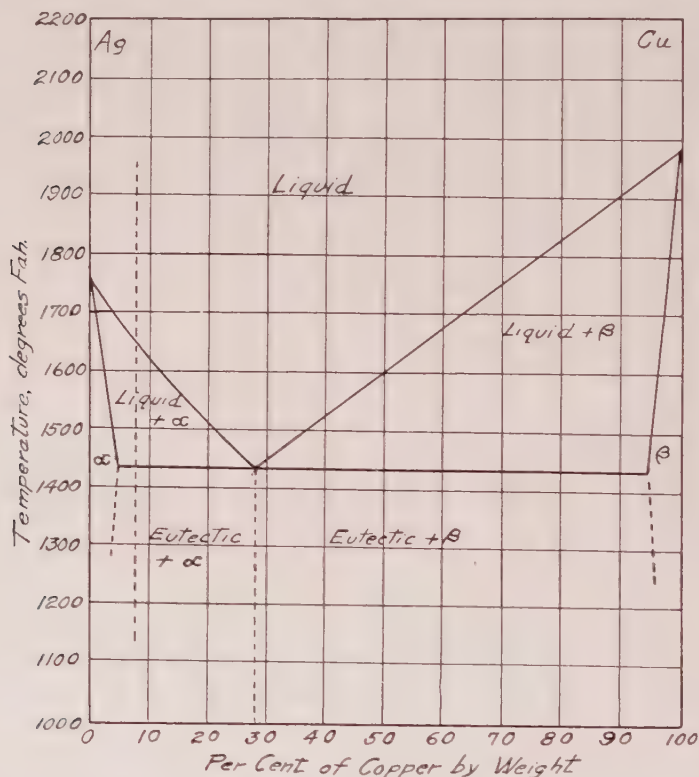


FIG. 1.—SILVER-COPPER EQUILIBRIUM DIAGRAM.

7.5. It is customary to designate the proportion of silver by parts per thousand, therefore sterling is called 925 thousandths fine. This silver fineness is fixed by law and only alloys containing this proportion of silver can be stamped "sterling." The remaining percentage may be copper or any other metal. In the United States, the use of sterling silver is confined almost entirely to the manufacture of silverware and jewelry, as our coinage is only 900/1000 fine.

Copper is the base metal of the sterling silver considered here. The equilibrium diagram of the silver-copper alloys is given in Fig. 1. Rob-

erts-Austen⁵ and Heycock and Neville⁶ originally determined the melting points of a series of alloys upon which this diagram is based. The eutectic has the approximate composition of 72 per cent. silver and 28 per cent. copper. As it has been generally assumed that silver will hold 5 per cent. copper in solid solution and copper will hold 5 per cent. silver in solid solution, these solid solubility limits are shown by dotted lines, but the authors' experience raises some question as to the accuracy of this assumption. Using this diagram, however, as a basis and a similar method of computation given by Jeffries and Archer,⁷ we find that sterling silver contains 11 per cent. eutectic and 89 per cent. solid solution. The eutectic contains 72 per cent. silver and 28 per cent. copper and the solid solution 95 per cent. silver and 5 per cent. copper.

MELTING AND CASTING

Sterling silver is melted usually in ordinary graphite crucibles, using gas, coke or oil as fuel. There is no accepted temperature at which the metal should be poured. The melting point of sterling silver is 1640°F., and pouring temperatures ranging from 1850°F. to 2300°F. are used. The temperature of the mold, method of pouring and rate of chill, are all variables that have to be considered with the temperature of the metal, but in general, experience indicates that when other conditions are properly controlled, temperatures between 1900° F. and 2000° F. will produce sound castings. Metal to be used for making rolled sheet or wire is poured into cast-iron molds similar to those used in the brass industry.

The weight of individual melts varies widely, but in large-scale production, ingots are made weighing approximately 1000 troy ounces. A typical ingot weighing approximately 1000 oz. will be 10 in. wide, 18 in. long and $1\frac{1}{8}$ in. thick, which makes a convenient size for rolling wide sheets. For narrow sheets, ingots are made from 5 to 7 in. wide by 24 in. long and $1\frac{1}{8}$ in. thick. Wire bars are cast in either circular or square cross-sections and weigh from 50 to 150 troy oz. For those accustomed to think in avoirdupois weight, the number of troy ounces divided by 15 will give the approximate avoirdupois pounds, the actual number of troy ounces in an avoirdupois pound being 14.583.

The operations of melting and pouring require careful regulation if sound ingots are to be produced, as the alloy is especially sensitive to oxidizing or reducing atmospheres. Various fluxes and so-called deoxi-

⁵ W. C. Roberts-Austen: Alloys. *Jnl. Royal Soc. of Arts* (March 1897).

⁶ C. T. Heycock and F. H. Neville: Complete Freezing Point Curves of Binary Alloys Containing Silver or Copper Together with Another Metal. *Phil. Trans. Royal Soc. of London* (1897) **189-A**, 25.

⁷ Zay Jeffries and R. S. Archer: *The Science of Metals*, 299, 1924. New York. McGraw-Hill Book Co., Inc.

dizers are used for correcting poor metal, but proper control of the conditions under which the melting and casting is done is the best assurance of success.

ROLLING

After the ingots are removed from the molds, they are cleaned, and in order to insure a surface free from scale, it is customary to overhaul them before rolling. This overhauling also allows a better inspection of the ingot for pinholes or other defects.

The amount of reduction at a pass and the total reductions between anneals are dependent upon the size of the rolling equipment. The procedure outlined in this paper is based on a breaking-down mill having rolls 19-in. diameter by 32-in. face, driven by a 150-hp. motor; a running-down mill 18 by 30 in. driven by a 75-hp. motor, and a finishing mill 18 by 30 in. driven by a 75-hp. motor. The overhauled bar is reduced from a little over 1 in. in thickness to $1\frac{1}{2}$ or $3\frac{3}{8}$ in. before annealing, about nine passes being required for this reduction. Bars not exceeding 14 in. in width are rolled to $3\frac{3}{8}$ in. and wider bars to $1\frac{1}{2}$ in. After annealing at $3\frac{3}{8}$ in., the narrower bars are rolled to a minimum of #14 B & S gage, which requires from 10 to 14 passes, depending on the width. The wide bars are rolled from $1\frac{1}{2}$ in. to #4 B & S, then annealed; then rolled to #10 B & S, annealed and rolled to #14 B & S. From #14 B & S, the reductions between anneals will run from 40 to 50 per cent.

Table 1 shows the hardening effect of cold rolling.

TABLE 1.—*Hardening Effect of Cold-rolling Sterling Silver*

Gage, Inches	Scleroscope*		Rockwell $\frac{1}{16}$ -in. Ball 100-kg. Load	
	Hard	Annealed	Hard	Annealed
As Cast	15		25.0	
0.375	28	18	77.0	42.0
0.065	36	16	86.0	31.0
0.032	30	18	79.0	43.0
0.015	28	12-13	77.0	15.0
0.008	23	11-12	65.0	10.0
0.005	20	12	52.0	10.0

* Universal Hammer.

^a Rockwell tests on thin metal show wide variations. These empirical figures are based on a large number of determinations.

ANNEALING

Annealing is done in muffle furnaces heated by gas, oil or electricity. Experience has shown that temperatures above 1000° F. are necessary for softening at a reasonable rate and in consequence, when the annealing is

done in open furnaces or exposed to the air, the surface is rapidly blackened by oxidation of the copper. In the silversmithing industry, this oxidation is called "fire" and stock which has been protected from oxidation during annealing is called "fireless." After annealing, the metal is dipped in a dilute solution of hot sulfuric acid, containing from 5 to 10 per cent. acid, and the black copper oxide is dissolved, leaving a white matte surface.

In order to prevent this oxidation, various types of sealed muffle furnaces are in use and the annealing is done in an atmosphere from which the air is excluded. Walker⁸ conducted some experiments from which he concluded that the best results are obtained when the annealing is done in a closed muffle filled with producer gas. Experience has shown that a water-sealed furnace using a steel retort into which a small amount of steam is constantly injected allows the annealing to be done at a temperature of 1200° F. with no appreciable oxidation.

The pickling in sulfuric acid removes only part of the oxide and the silversmith is compelled to resort to a "fire dip" (1-1 nitric acid) to remove the last traces, or else cut off the surface to a sufficient depth to get below the scale. Either operation is relatively expensive and removes considerable silver which afterwards has to be reclaimed. The depth of penetration of this oxidation depends on temperature, time and degree of exposure to the air. In order to obtain some idea as to the rate of oxidation during annealing, the following tests were made on a number of specimens.

Samples of sterling silver, free from oxygen, were heated in an alundum boat filled with finely ground alumina so that only one surface was exposed to the air. There was some slight oxidation of the lower surfaces. These specimens were weighed before and after each anneal and air was blown over the surface during annealing, in order to accelerate the action. In order to form some basis for comparison, it was assumed that the action of the air would oxidize the copper to cupric oxide. Theoretically, $\frac{1}{10}$ mg. of oxygen will oxidize 0.397 mg. of copper to cupric oxide. It follows, therefore, that if we multiply the increasing weight during any given anneal by the factor 0.397, we will obtain the weight of the copper that is oxidized. This value divided by the total weight of copper in the specimen will give the percentage of the copper oxidized, and this percentage multiplied by the gage of the metal will give the average depth to which the oxygen had penetrated. The specimens used for this test had a fineness of 926.8 parts per thousand; they were all from the same bar but were rolled to different gages. The tests were conducted on a large number of specimens at temperatures ranging from 1200° F. to 1400° F.

⁸ W. H. Walker: Annealing Sterling Silver. *Jnl. Amer. Chem. Soc.* (1909) 29, 1198.

The diagram on Fig. 2 shows the results obtained at 1200° F. and 1400° F. As would be expected, the gage had little effect and the curves show the average values for all gages at the different temperatures. The most noticeable fact is the very rapid increase in rate of oxidation when the temperature is raised from 1200° F. to 1400° F., particularly during the first half hour.

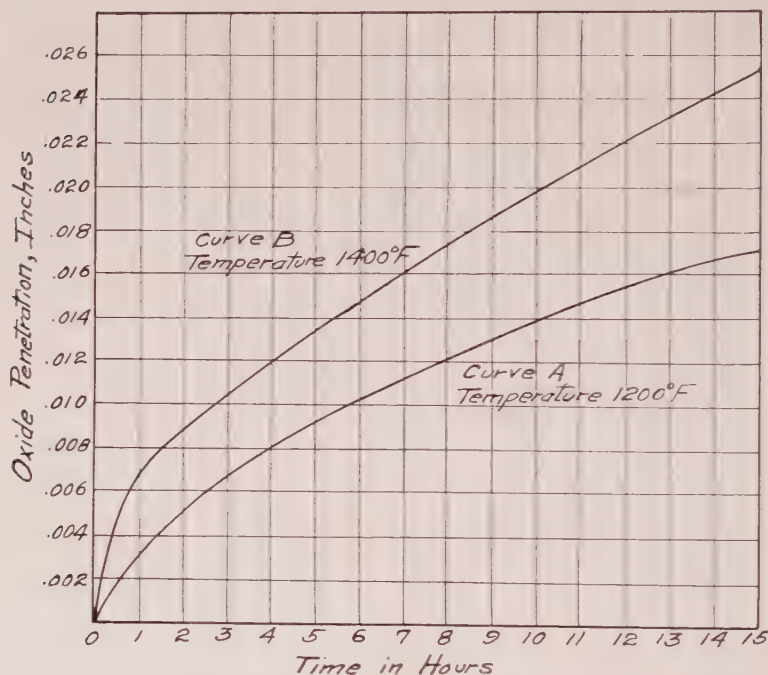


FIG. 2.—OXIDATION OF STERLING DURING ANNEALING IN AIR.

PHYSICAL CHARACTERISTICS

As already explained, the first debasement of silver with copper was simply to give it strength and resistance to wear and to make an alloy suitable for coinage purposes. Silversmiths found that this same composition gave them an alloy of considerable intrinsic value, as well as the necessary malleability and ductility for easy working into artistic patterns, and enabled them to produce finished articles of sufficient hardness and strength to resist ordinary wear.

Until comparatively recent years, silversmithing was mostly done by hand and the craftsman had no particular interest in knowing the limits of the physical properties; for example, when forming a piece of hollow ware, he would carry the work to the point where his experience indicated that annealing would be beneficial, and he conducted all of his operations well within the safe working limits of the alloy. With the

substitution of machinery for hand labor a more careful analysis of the physical properties has become important.

There are two main classifications of sterling silver stock: flatware and hollow ware. The first class includes the relatively heavy stock from about 14 B & S gage and thicker, which is used for spoons and forks.

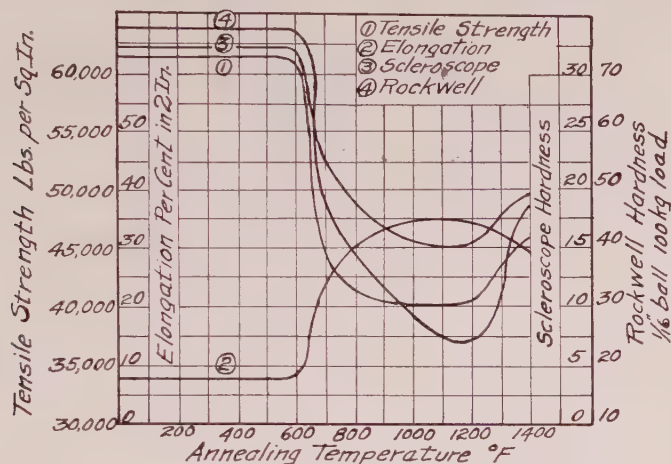


FIG. 3.—PHYSICAL PROPERTIES OF AIR-COOLED STERLING.

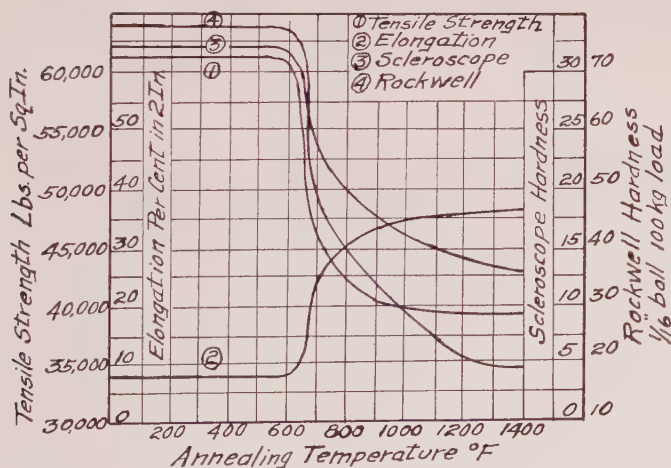


FIG. 4.—PHYSICAL PROPERTIES OF QUENCHED STERLING.

Hollow ware is thinner stock used for cups, vases, plates, cases, trays and similar articles. Tubing is made from disks cut from flatware stock and drawn to the required size. Spoons and forks are rough-blanked from heavy sheet, then hammered or grade-rolled and passed through successive blanking and stamping operations to the finished article. Hollow ware is stamped, drawn, spun or hammered to the shape desired.

In addition to cold working, hollow ware is also subjected, in many instances, to soldering operations. Therefore, if machinery is to be used in the various operations, an accurate knowledge of physical properties is necessary if the greatest economy of production is to be effected.

The following data are the results of investigations conducted at the plant of Handy and Harman over a period of years. From a strictly scientific point of view, much work remains to be done, but the authors feel justified in presenting this contribution to the general knowledge of the more important physical properties of sterling silver.

Fig. 3 is a diagram of the tensile strength and hardness of sterling silver 0.065 in. thick after annealing for one hour at temperatures from 600° F. to 1400° F. The values shown in Fig. 3 are based on air cooling to

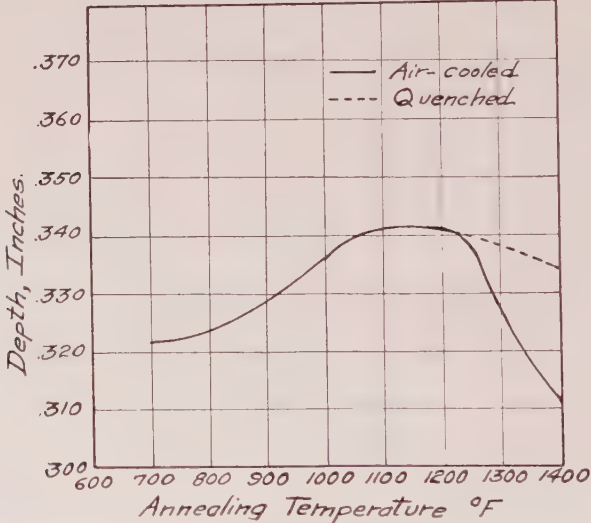


FIG. 5.—OLSEN CUPPING TEST.

approximately room temperature. Fig. 4 shows the same physical properties as Fig. 3 but the stock is quenched at the annealing temperature. These diagrams show that for practical purposes a temperature of 1200° F. will satisfactorily anneal sterling silver. They also show some wide differences in physical properties between air-cooled and quenched sterling silver when annealed at temperatures above 1200° F. Further investigations as to the exact cause of these differences are being conducted.

The ductility of sterling silver is relatively high and Fig. 5 shows the results of cupping tests made with a standard Olsen machine. The specimens were all 0.065 in. thick and the annealing period was one hour. It is interesting to observe the difference between air-cooled and quenched sterling silver at the higher temperatures. The grain produced by

cupping is noticeably coarser at temperatures above 1300° F., particularly in the case of the quenched stock.

METALLOGRAPHY

Etching.—Although alkaline copper-ammonium chloride and ammonium persulfate are sometimes recommended for etching sterling, heat-tinting has been found to be the most satisfactory means of developing the structure of the silver-copper eutectic. Neither one of these etching reagents nor the heat-tinting process will bring out the structure of the solid solution. The authors have had the best success in etching the solid solution with the mixture of chromic acid and potassium dichromate described below. This reagent was brought to our attention by E. A. Anderson, who used it in connection with some metallographic investigations of pure silver at the Hammond Laboratory, Yale University.

Solution A—Potassium dichromate.....	2 gm.
Nitric acid (1:1).....	100 c. c.
Solution B—Chromic acid.....	20 gm.
Sodium sulfate.....	1.5 gm.
Water.....	100 c. c.

Solution A is diluted to 20 volumes and an equal volume of Solution B is added. When properly mixed and applied with a camel's-hair brush, a red silver chromate should form; this remains granular and does not adhere to the surface of the specimen. If the chromate adheres, more Solution A should be added, and if no chromate forms, more of Solution B is needed.

Description of Photomicrographs

A magnification of 200 × was used for all photomicrographs given in this paper. Unless otherwise stated, the specimens were cooled in air.

Fig. 6 shows a heat-tinted specimen with the structure typical of cast sterling. The dark irregular portions are the eutectic, which under higher magnification may be seen to have the lamellar structure characteristic of eutectics. In Fig. 7, the cast structure has been developed by etching.

Figs. 8 and 9 show heat-tinted and etched specimens of cold-rolled sterling. It is difficult to distinguish between annealed and cold-rolled sterling under the microscope at ordinary magnification, as the directional properties imparted to the eutectic by rolling are retained after annealing; and the grain size of the solid solution is too small for the distortion of the crystals to be detected. Figs. 10 to 15 show the normal structure of annealed sterling. These photomicrographs are not radically different in appearance from Figs. 8 and 9.

At 1300° F. there is a marked growth in the grain size but no apparent alteration in the amount or distribution of the eutectic, though it is at

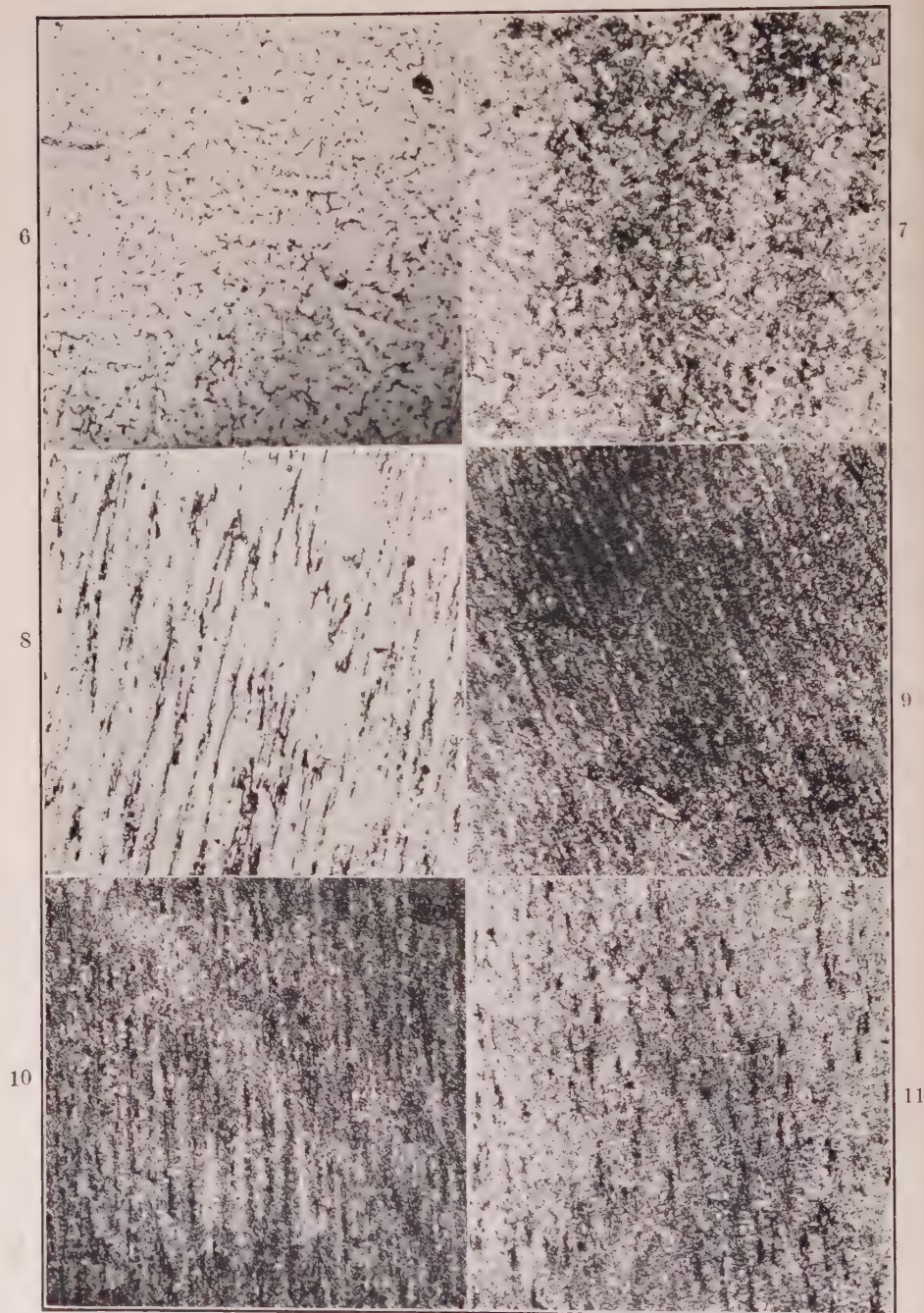


FIG. 6.—CAST BAR, HEAT-TINTED. $\times 200$.

FIG. 7.—CAST BAR, ETCHED. $\times 200$.

FIG. 8.—HARD STERLING, 0.065-IN. GAGE AFTER 42 PER CENT. REDUCTION BY ROLLING. HEAT-TINTED. $\times 200$.

FIG. 9.—HARD STERLING, 0.065-IN. GAGE AFTER 42 PER CENT. REDUCTION BY ROLLING. ETCHED. $\times 200$.

FIG. 10.—ANNEALED AT 700° F. FOR ONE HOUR. HEAT-TINTED. $\times 200$.

FIG. 11.—ANNEALED AT 700° F. FOR ONE HOUR. ETCHED. $\times 200$.

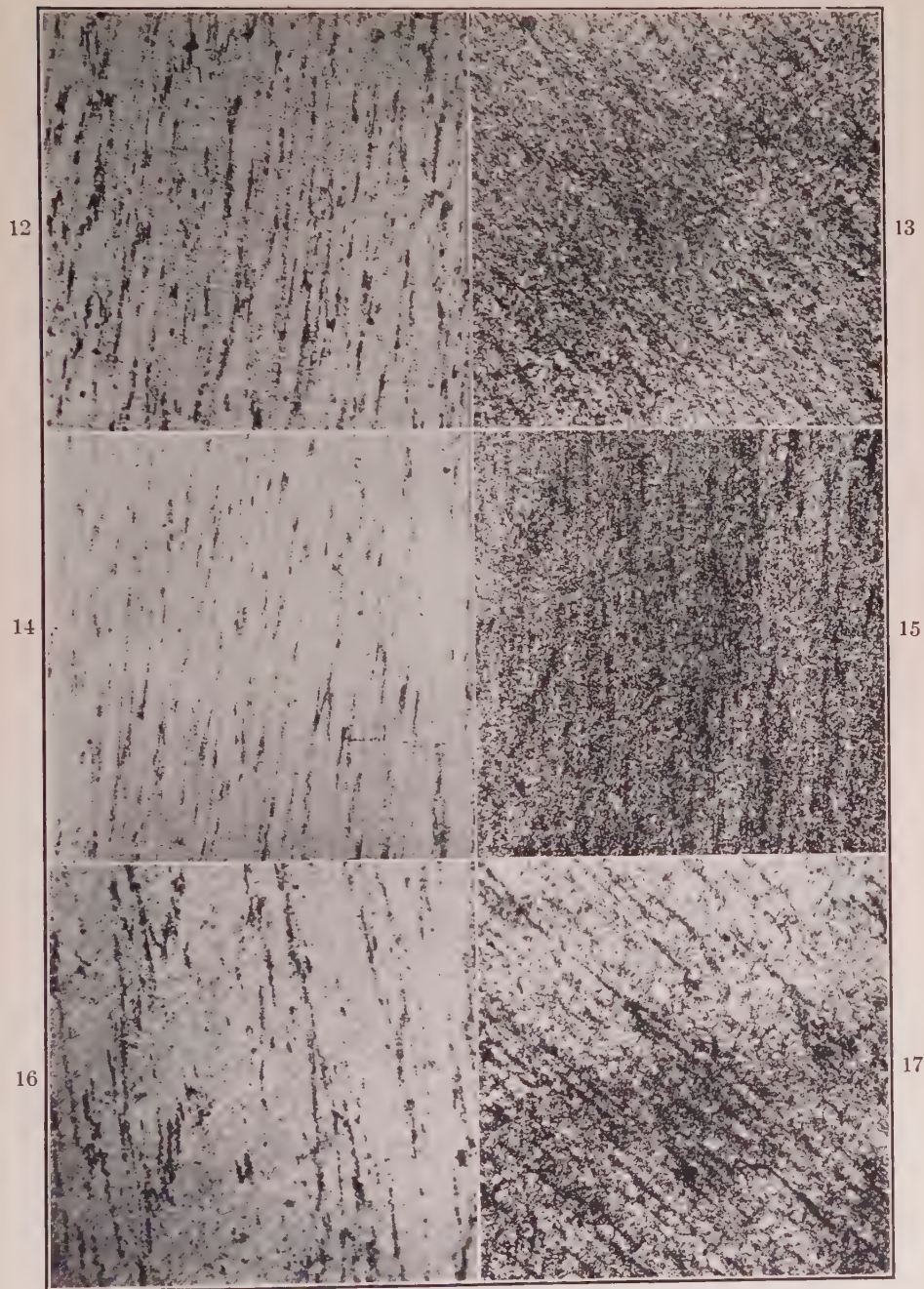


FIG. 12.—ANNEALED AT 1100° F. FOR ONE HOUR. HEAT-TINTED. $\times 200$.
 FIG. 13.—ANNEALED AT 1100° F. FOR ONE HOUR. ETCHED. $\times 200$.
 FIG. 14.—ANNEALED AT 1200° F. FOR ONE HOUR. HEAT-TINTED. $\times 200$.
 FIG. 15.—ANNEALED AT 1200° F. FOR ONE HOUR. ETCHED. $\times 200$.
 FIG. 16.—ANNEALED AT 1300° F. FOR ONE HOUR. HEAT-TINTED. $\times 200$.
 FIG. 17.—ANNEALED AT 1300° F. FOR ONE HOUR. ETCHED. $\times 200$.

this temperature that a decided change in the physical properties of sterling may be seen in Fig. 3. Above 1300°F . the eutectic is rapidly absorbed by the solid solution, leaving the crystals free to grow without obstruction. As mentioned before, the investigation of the effect of heat treatment on sterling silver within this range is not complete, but the

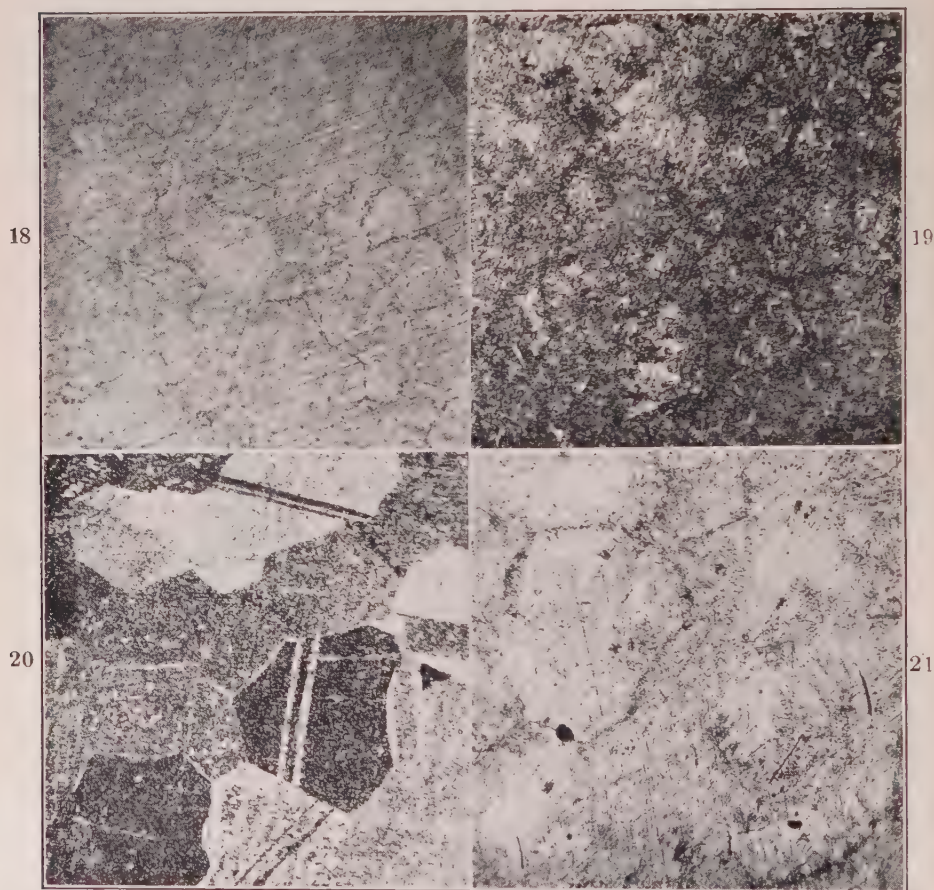


FIG. 18.—ANNEALED AT 1400°F . FOR ONE HOUR. HEAT-TINTED. $\times 200$.

FIG. 19.—ANNEALED AT 1400°F . FOR ONE HOUR. ETCHED. $\times 200$.

FIG. 20.—QUENCHED FROM 1450°F . ETCHED. $\times 200$.

FIG. 21.—AIR-COOLED FROM 1450°F . ETCHED. $\times 200$.

experiments already conducted lead the authors to believe that the solubility of copper in silver at 1400°F . is much greater than the equilibrium diagram indicates. If the copper in a sterling alloy was completely miscible in silver at 1400°F ., the temperature of incipient fusion would be raised. The belief that this occurs is strengthened by the fact that in the manufacture of sterling articles silversmiths use silver solders that

require temperatures of over 1450° F. for complete liquefaction. Further confirmatory evidence is presented in Figs. 20 and 21. These specimens were quenched and cooled slowly in air after an anneal of one hour at 1450° F. To conform with the equilibrium diagram, approximately 15 per cent. of the alloy should be molten at this temperature, but this is not the case. It is expected that the investigation of the solubility relationships of silver and copper will explain many of the peculiarities of sterling encountered by manufacturers of sterling silverware.

DISCUSSION

O. W. ELLIS, East Pittsburgh, Pa. (written discussion).—About four years ago the writer had occasion to conduct an investigation of the hardening power of sterling silver and in this connection obtained a number of results, which may be of interest as enlarging upon that section of the paper devoted to the subject of rolling. Two alloys were studied—one a sterling silver such as is described in the paper, the other a special silver containing cadmium.

Small ingots were cast of these two alloys, the ingots being $\frac{1}{4}$ in. thick. These, after trimming, were reduced in 18 passes to a thickness of 0.03 in. Brinell hardness tests were made on the alloys, a $\frac{1}{4}$ -in. ball being used under a load of 540 kg. The following results were obtained:

	SPECIAL SILVER	STERLING SILVER
As cast	57	109
PER CENT. REDUCED IN THICKNESS		
10.6		119
14.3	109	
17.0		158
22.4	143	
29.8		175
32.7	150	
40.4		194
44.9	143	
53.2		185
55.1	158	
59.6		185
61.3	158	
70.1		185
79.6	194	
80.8		206

Check tests were made on another ingot of the special silver with the following results:

As cast	57
PER CENT. REDUCED IN THICKNESS	
19.6	98
30.8	148
40.4	156
50.0	154
60.0	162
70.0	166
70.8	181

The results of these tests are presented graphically in Fig. 22.

It may be of interest to note that the Brinell hardness numbers of sterling silver knife blades such as are used for cutting fruit, etc. tested by the writer lie in the neighborhood of 150 at the heavier sections of the blades and increase somewhat towards the cutting edges of the blades.

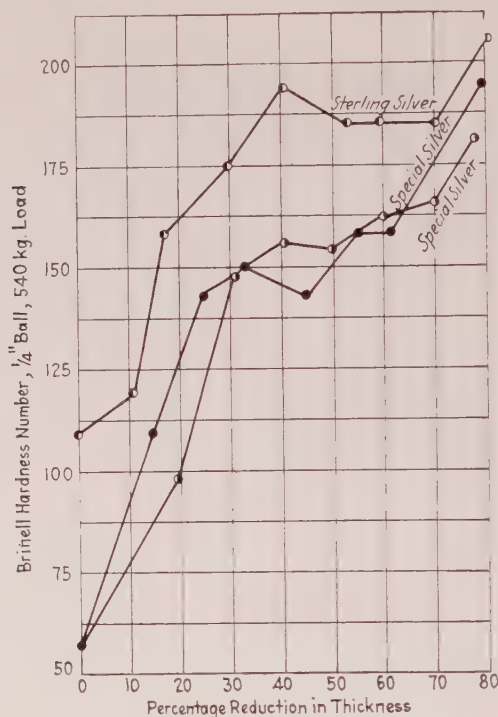


FIG. 22.

J. B. WATERFIELD, Attleboro, Mass.—I have found in considerable practice that temperatures over 2200° F. give me much better working conditions in processing, especially in reference to silver that has to be severely spun or drawn.

In reference to annealing, 1200° C. is altogether too high for deep drafting. There or four years ago, I spent about six months with a double chamber furnace, using very hot steam with three pyrometers to get a close check, and the temperature of between 950° and 1000° F. gave me a sufficient softening to get desired results from 1150° to 1200° F.

In reference to any temperature over 1200°, I found that the silver would not stand any pronounced punishment; that is, on a piece of hollow ware that had to have a very severe edge turned (what we term in the trade a square, o. g.), you would find it exceedingly difficult to make that bend if the temperature went much over 1200°.

C. S. SMITH, Waterbury, Conn.—I would like to ask the authors if they have tried cathodic etching for developing the microstructure of the alloys. This process, which I described in a paper before the British Institute of Metals last year,⁹ consists essentially of making the specimen the negative electrode for the passage of an electric

⁹ *Jnl. Inst. Metals* (1927) **38**, 133.

discharge through a gas (usually air) at low pressure. This method works extremely well on copper-silver alloys of duplex structure, and gives excellent contrast between the copper and silver-rich solid solutions.

F. E. CARTER, Newark, N. J.—This paper is of interest to anybody working in sterling silver. We note in the first table the softening effect of cold rolling on sterling silver. We also can confirm the unexpected change in hardness, etc., at 1200° F. as given in Fig. 3 for the air-cooled alloy. I want to thank Mr. Leach, too, for publishing this etching agent. We have already proved its value. Until we tried it our photomicrographs were even worse than Mr. Leach's Figs. 6 to 17. But if those photomicrographs do not tell us much, certainly Figs. 18 to 21 are really important, showing the solubility of copper in silver at 1400° F. to be greater than the Heycock-Neville diagram gives.

B. EGEBERG, Meriden, Conn.—The authors say that the molds are of the same type that are used in the brass foundries and they might be 10 in. wide, 18 in. long and $1\frac{1}{8}$ in. thick. I would like to ask if the authors have had any experience with ingots of that type bridging over somewhere between the bottom and the top before the metal has cooled down, leaving the possibility for shrinkage cavities below the top. The tool-steel manufacturer, by hot working, can weld small cavities, but even then he uses a tapered ingot, large end up, hoping at least to locate the cavity at the top.

The non-ferrous manufacturer works the ingots mostly cold and has therefore only small opportunity to weld cavities. It seems, therefore, that some benefit might be obtained by transferring the steel man's experience to the non-ferrous field.

E. M. WISE, Bayonne, N. J.—I would like to confirm the observations of the authors regarding the variation with the temperature of the solubility of copper in silver, and would add that considerable change in solubility occurs below 1200° F. This change in solubility renders possible the age hardening of these alloys. Some experiments carried out six years ago at the Wadsworth Watch Case Co. showed that quite pronounced age hardening could be effected. Standard sterling silver annealed and quenched from 650° C. showed the following properties: elongation, 42 per cent.; yield point, 19,680 lb. per sq. in.; ultimate tensile strength, 37,400 lb. per sq. in. The same alloy after quenching from 650° C. and aging at 325° C. for 30 min. showed the following properties: elongation, 26 per cent.; yield point, 30,000 lb. per sq. in.; ultimate tensile strength, 43,400 lb. per sq. in.

An aluminum content alloy was developed which showed much greater strength after age-hardening. This alloy (Ag, 92.5; Al, 4; Cu, 3.5) when quenched from 650° C., showed the following properties: elongation, 55 per cent.; yield point, 19,820 lb. per sq. in.; ultimate tensile strength, 51,600 lb. per sq. in. The same alloy after quenching and aging at 325° C. for 30 min. showed the following properties: elongation, 12.5 per cent.; yield point, 69,300 lb. per sq. in.; ultimate tensile 77,800 lb per sq. in.

E. A. CAPILLON, Attleboro, Mass.—We have found the addition of 0.5 per cent. of copper phosphorous very beneficial in the melting of sterling silver. We make rolled sterling plate in which the sterling is soldered on to a base metal. When this composite plate has been rolled down to about 0.020 in., the silver may be not exceeding 0.003 or 0.004 in. thick. At that point, the silver plate after annealing is very much pitted and full of small blisters and streaks. We have found that adding 0.5 per cent. of copper phosphorus containing 15 per cent. phosphorus reduces pitting to the vanishing point, and the plate obtained is extremely smooth instead of being rough, as in the former case.

We also obtained the same results as Mr. Leach relative to annealing; for the air-cooled specimens, the minimum hardness was at 1200° F.

R. H. LEACH.—Mr. Waterfield has made some very positive statements which are seemingly contradictory to the results we have obtained in our own practice. I still feel that, from our experience, a temperature of 1200° F. is a proper annealing temperature for sterling silver. There may be special cases where this particular low temperature will be beneficial. I am not prepared to say. Time is an element and all metallurgical reactions are time and temperature reactions. It is necessary in commercial work to compromise on the time and temperature.

R. H. LEACH (written discussion).—The authors appreciate the interest shown in the paper and the contributions by various members. This added information, with the exception of the remarks by Mr. Waterfield, is in general agreement with the authors' own experience.

The Platinum Metals and Their Alloys

BY FREDERIC E. CARTER,* NEWARK, N. J.

(New York Meeting, February, 1928)

THERE have been many attempts to prove that platinum was known to the ancients, but since no traces of the metal have been found in the relics of early times, it must be concluded that it was not known to them. As far as records go, it was actually first discovered in the 16th century in a Spanish mine on the Pinto River in South America; from which source it received its name of *Platina del Pinto* (little silver from the Pinto). It was more or less of a rarity and was a subject of interest to a few chemists only, until the year 1822 when the metal was first discovered in Russia. In 1819 there were noticed in the washings of the gold sands of the southern part of the Ural Mountains, grains of a heavy white substance, but it was not until three years later that this substance was found to contain platinum. While at first the amounts of platinum brought from the Urals were meager, prospecting soon disclosed rich deposits extending over a considerable area, and nuggets from 10 to 20 lb. were by no means rare. This discovery assured to chemists an ample supply of platinum for their crucibles, etc.

The ore is now found in various parts of the world but the richest deposits are still found in the Ural Mountains. The platinum of commerce is obtained entirely from alluvial deposits at depths varying from 6 to 40 ft. The sand and gravel of former river beds are subjected to a series of screenings and washings to effect the separation of the ore. Actually, probably all gold-bearing gravel beds of the world contain platinum, and it is more than likely that large quantities of platinum ore have been thrown away with the black sand washings from gold placer deposits. This is especially true of the alluvial deposits of the Pacific Coast in California and Oregon.

Platinum ore is usually found in the form of rounded or flattened grains of "sand," and occasionally in irregular lumps of the size of peas. Large nuggets are very rare. The ore has a metallic luster and is distinguished by its steel gray color, but shows light gray streak when rubbed on a hard white surface; it has a high specific gravity, 16 to 19; is infusible in the hottest blast furnaces, and insoluble in any single acid. Platinum ore is a complex body consisting of the metal in combination with varying proportions of the other members of the platinum group; iridium,

* Research department, Baker & Co., Inc.

rhodium, palladium, ruthenium and osmium, together with from 4 to 20 per cent. of iron. In alluvial deposits, the ore is generally associated with iridosmium (the native alloy of iridium and osmium possessing a hardness superior to hard tempered steel), magnetic iron and sand, garnierite, epidote, and often with zircon, zirconite, ilmenite, peridot, quartz, diamond and chrysolite.

Dr. J. M. Hill gives the following "Hints for Prospectors of Platinum:"¹

"The placer deposits containing platinum are all, so far as known, in the vicinity of areas of basic igneous rocks, and it would seem that in any search for new deposits of platiniferous gravels the first step is the search for outcrops of peridotite, pyroxenite, dunite, and serpentine. When areas of these rocks have been found, the gravels of the streams rising in them should be washed to ascertain if platinum is present. The heavy concentrates found in gravels carrying platinum are usually rich in chromite and olivine. The character of the rock particles often gives a clue to the source from which the gravels were derived.

"Crude platinum, as it occurs in placer concentrates, is ordinarily a silvery white metal which could be confused only with silver and possibly pieces of iron or steel. It can be distinguished from both of these metals, as they are soluble in dilute nitric acids; crude platinum can be dissolved only in concentrated aqua regia, a mixture of 3 parts of hydrochloric (muriatic) acid and 1 part of nitric acid.

"In some placer deposits the grains of platinum are coated with a dark film and somewhat resemble the grains of the dark minerals chromite, magnetite, or ilmenite, from which they are separated by careful panning, as the specific gravity of platinum is greater than that of any of those minerals.

"Platinum will not amalgamate with quicksilver alone, but will amalgamate if sodium is added. In ordinary quicksilver amalgamation the flakes of platinum float on the surface and can be removed. If sodium amalgam is used, the platinum may be separated from gold by agitating the amalgam with water until all the sodium is used up to form sodium hydroxide; then the platinum will come out on the surface of the amalgam, provided, of course, the amalgam is sufficiently liquid.

"Platinum has a hardness of 4-5, and can be scratched with a knife. It is so malleable that it can be pounded without heating into very thin sheets. It is practically infusible; the grains can not be melted together, as particles of gold can.

"A relatively simple chemical test can be made to determine the platinum. The metallic particles are dissolved by boiling in concentrated aqua regia and the resulting solution is allowed to remain on the stove till dry. The residue is dissolved again in hydrochloric acid and evaporated by boiling till the solution is thick but not quite dry. This mass is dissolved in distilled water and a few drops of sulphuric acid and of potassium iodide solution are added, which, in the presence of platinum, causes the solution to turn a very characteristic wine-red, if much of the metal is present, or to a reddish pink in the presence of small quantities of platinum.

"The test outlined above is fairly delicate, but it can be used to detect traces of platinum in the presence of large quantities of iron or other elements.

"A second test may be applied to the aqua regia solution after the resolution in hydrochloric acid outlined above. In this test potassium chloride (KCl) is added to the solution, which precipitates yellow crystals of potassium platonic chloride K_2PtCl_6 if platinum is present.

¹ Mineral Resources for 1916. Pt. 1, Metals.

"A third test may be applied. Add ammonium chloride (NH_4Cl) to the aqua regia solution, which will precipitate yellow crystals of ammonium platinic chloride, if platinum is present.

"The precipitates from tests 2 and 3 are both insoluble in alcohol but are soluble in water and may be reduced to platinum sponge by heating.

"All these tests are comparatively simple and positive when made on single grains, but they can not be relied upon when various other elements are present in the material tested. It is, therefore, recommended that their use be restricted to grains of a single mineral picked from the concentrates obtained by panning a sample of either rock or gravel."

One of the more important sources of the present day of platinum metals is the nickel industry in Canada, several thousand ounces of both platinum and palladium being recovered annually, but only small amounts of the other members of the group are obtained. This is obtained in the refining of the nickel-copper mattes, which result from the smelting of the nickel ores.

Metallurgy.—The crude platiniferous materials obtained by the screening and washing consist of two constituents: *a*, the platinum ore proper, containing about 80 per cent. platinum, the other metals of the group being present in small quantities only; *b*, osmium-iridium, the main contents of which are osmium, iridium, ruthenium, while the other metals of the group constitute only a small percentage. Constituent *a* is soluble in aqua regia, *b* is practically insoluble.

The crude platinum is crushed fine and treated with aqua regia; the platinum goes into solution and from this is precipitated as ammonium-platinum chloride, which on heating to redness gives platinum sponge. The metals resemble one another very closely and the methods employed vary with the proportion in which the individual metals are present in the material. As a rule a combination of dry and wet processes has to be used. It may be stated that the property, possessed by osmium and ruthenium, of forming volatile tetroxides is made use of for separating them from the other four platinum metals. The preparation of the pure platinum metals from the commercial grades constitutes one of the most difficult problems of inorganic chemistry, and naturally the methods used are kept secret by the refineries.

Melting.—The platinum metals are generally melted by means of coal gas and oxygen or hydrogen and oxygen in a lime crucible; lime was first used for this purpose by Deville and Debray and its use has continued to this day because, having a very high fusing point, being a good heat insulator, and absorbing many of the impurities in the platinum, it has proved superior to other refractories. Great improvements in the form of the furnace have of course been made and careful control of the gas composition is necessary, since the platinum metals are very sensitive to gases; the writer has described elsewhere some of the troubles caused

by improper melting.² Small melts are made in the so-called Jeweler's Sand Crucible, but the larger quantities, say $\frac{1}{2}$ to 25 kg., are melted in lime. The Ajax-Northrup high-frequency induction furnace has proved useful in melting platinum metals as intensely high temperatures are rapidly obtained and it allows melts to be made in any atmosphere or *in vacuo*.

Working.—Ingots of platinum and its alloys are usually worked at a bright red heat until they have undergone considerable reduction; thereafter cold rolling or cold swaging and drawing methods are used. Like other metals platinum hardens up on working, not so fast as copper but faster than gold or silver, and must be annealed. Generally speaking, platinum and platinum alloys require temperatures of 1000 to 1200° C. for annealing; the addition of iridium causes an increase in the requisite temperature: for example, 650° C. is sufficient for pure platinum, 1000° C. for commercial platinum, 1100° C. for 5 to 15 per cent. iridio platinum, and 1200° C. is necessary when the iridium content is higher than 15 per cent.

The metal is easily spun and spinning is therefore resorted to in manufacturing articles of varied shapes. Seamless tubing is readily made. Platinum "drags" somewhat in punch presses and does not cut cleanly in the lathe, acting like soft copper in this regard.

Soldering and Welding.—Fine gold is the most usual solder for the platinum metals; sometimes higher fusing solders are necessary and then ternary alloys of gold, silver and palladium are often used, the amount of palladium determining the melting point. Platinum welds very nicely either electrically or by the oxyhydrogen flame; it is also quite simple to weld two pieces of platinum together by hammering them together at a fair red heat.

PROPERTIES

It is not proposed to give here the chemical properties of the metals of the group, a considerable amount of information having been published on the chemistry of the platinum metals, and the reader is referred to the standard publications. The physical properties have also been given at various places but it is thought best to assemble available reliable information in tabular form, together with some properties determined in the writer's laboratory (Table 1).

PLATINUM METALS AND GASES

It is certain that up to the present day it has not been fully realized how important are the effects of gases on metals, but we are beginning to learn that the properties we have associated with many of the metals

² F. E. Carter: Some Notes on the Metals of the Platinum Group. *Trans. Amer. Electrochem. Soc.* (1923) **43**, 397.

hold true only for gas-saturated material and not for the pure metal itself. Generally speaking, however, the vacuum-melted, vacuum-poured and vacuum-annealed metal is of academic interest only because such special treatment is hardly feasible in commercial work, but it certainly should be recognized that the properties we associate with metals are for the metals in commercial form, *i. e.*, for alloys of metals and gases. These remarks may not apply to all metals but they certainly do in the case of the platinum metals.

We all know the extreme reactivity between the platinum metals and the various gases and the voluminous literature testifies to the interest in the subject; furthermore, it may be stated that this literature in addition to being most voluminous is most contradictory and generally most unsatisfactory. It would have been more discreet to have omitted this paragraph but the writer feels that something should be stated on the subject in a general paper on the platinum metals, if only to mention that we know very little about it with any certainty. There are many reasons for this: One is that the metals all have high melting points and as the gas-metal phenomena have to be studied both in the solid and in the liquid state, experiments have to be made at high temperatures with the consequent difficulties due to containers, etc. The second difficulty is that the reaction between gas and metal is seriously affected by slight impurities in the latter; for example, the writer stated in a paper in 1923³ that palladium could not be melted under reducing conditions and yet in this paper he is going to add to the contradictoriness of this subject by saying that palladium *should* be melted with a highly reducing flame. Full reasons for this volte-face cannot be given here, but it should be related that the presence of a small quantity of another metal was the chief cause for the previous incorrect statement. Third, hydrogen is either absorbed or adsorbed by the metal or actually combines with it to form one or more hydrides whose ranges of stability are unknown. Fourth, each of the platinum metals appears to form numerous oxides which are capable of existence only within certain narrow limits of temperature.

For those who wish to learn more on this subject, reference is made to Friend's Textbook of Inorganic Chemistry (9, Pt. 1), where a summary is given together with numerous literature references.

This reactivity between the platinum metals and gases is undoubtedly the reason for their usefulness as catalysts; from what has been said on the possible changes going on when platinum metals are exposed to hydrogen or oxygen at varying temperatures the reason may readily be seen for the catalytic value of platinum, palladium, etc., in both reducing and oxidizing catalytic reactions.

³ *Loc. cit.*

TABLE 1.—Physical Properties of the Metals of the Platinum Group

	Pt	Ir	Os	Pd	Rh	Ru	Units
Atomic weight	195.2	193.1	190.9	106.7	102.9	101.7	Grams per c. c.
Specific gravity	21.40	22.42	22.50	12.16	12.44	12.10	° C.
Melting point ¹	1,755	2,350?	2,700?	1,550	1,950	2,450?	° C.
Boiling point ¹	4,300	>4,800	>5,300	2,200	>2,500	>2,700	× 10 ⁻¹⁰ mm. at 1000° K.
Vapor pressure ²	324						× 10 ⁻⁸ mm. at 2000° K.
	107						Mm. at 4180° K.
	760						At 20° C. Joules per gr. atom.
Comparative volatility in air at 1300° C. ³ ...	2	60	(1000)	6	1	200	0 to 100° C. Joules per gr. atom.
Specific heat ⁴	26.5			26.2			Kilojoules per gr. atom.
Latent heat of fusion at melting point ⁴	10.5	26.1	25	10.8	5.1	10	Kilojoules per gr. atom.
Latent heat of vaporization at boiling point ⁴	520	6	9	11.8	8.4	9.1	× 10 ⁻⁶ at 20° C.
Temperature coefficient of linear expansion ⁵	8.9	6.5	6.1	11.76	8.5	9.63	× 10 ⁻⁶ 0 to 100° C.
	8.84						× 10 ⁻⁶ 0 to 40° C.
	8.998						× 10 ⁻⁶ 0 to 300° C.
	9.14						× 10 ⁻⁶ at 1000° C.
	11.30						× 10 ⁻⁶ 0 to 1670° C.
	9.75						At 18° C.
Thermal conductivity	0.1664	0.111		0.1683	0.216		At 100° C.
	0.1733			0.182			
Hardness, Brinell:							Baby Brinell
Cast.....	50	172		52	139	220	2 mm. ball 120 kg. load
Hard.....	97			109			
Annealed.....	47			49			
Hardness, scleroscope:				25			
Hard.....	21			8			
Annealed.....	7			4.8			
Hardness, Mohs' scale.....	4.3						Diamond = 10
Ultimate strength:							Kg./mm. ² ; 0.5-mm. wire.
Hard.....	34			39			Kg./mm. ² ; 0.5-mm. wire
Annealed.....	15			14			Per cent. 2 in. length; 0.5-mm. wire
Elongation:				1.0			Per cent. 2 in. length; 0.5-mm. wire
Hard.....	0.8			24			
Annealed.....	32						
Young's modulus: ⁷							
Hard.....	17,000	52,700		12,000	30,000		Kg./mm. ²
Annealed.....	15,200			9,750			Kg./mm. ²
Rigidity, ⁸ cast.....	6.10			5.11			Dynes per sq. cm.
Poisson's ratio, cast	0.387			0.393			

Volume elasticity, ⁹ cast.	24.7			17.6		Dynes per sq. cm.
Erichsen ductility test:						
Hard.....	7.8			7.6		Mm.
Annealed.....	12.2			12.0		Mm.
Reflectivity (visible spectrum range) ¹⁰	0.62	0.64			0.68	0.520 μ
	0.65	0.66			0.70	0.576 μ
	0.68	0.68			0.71	0.680 μ
Emissivity ¹¹	0.38	0.38		0.38	0.29	0.55 μ solid
	0.33	0.33		0.33	0.29	0.65 μ solid
	0.38	0.38		0.37	0.30	0.65 μ liquid
Refractive index ¹²	1.17					0.257 μ
	1.94					0.441 μ
	2.63	2.13		1.62	1.54	0.579 μ
	2.91					0.668 μ
Absorption index ¹³	1.65					0.257 μ
	3.16			3.41	4.67	0.441 μ
	3.54	4.87				0.579 μ
	3.66			5.8	1.1	0.668 μ
Magnetic susceptibility, ¹⁴ H.....	1.32	0.15	0.04		0.56	$\times 10^{-6}$, Paramagnetic. Per gr.
Increase of resistance in magnetic field ¹⁵	0.0005					at 18° C.
Electrical resistance at 0° C., annealed.....	60.0	32.1	57.1	64.8	87.0	Per cent.; in field of 10,000
Hard.....	9.97	5.33	9.50	10.78	14.47	gausses.
Temperature coefficient of resistance per °C.: Annealed.....	0.003917			0.0037		Ohms per mil. ft.
Annealed.....	0.003923			0.00236		Microhms per cm. ³
Electromotive force against Pt at 1100° C. ¹⁶	0.00318	+14.5		-13.5	+15.8	0-100° C.
Velocity of sound:						0-100° C.
	2,690			3,150		M. v.
	2,570					At 20° C. meters per sec.
	2,460					At 400° C. meters per sec.
Cathode sputtering, relative rate ¹⁷	40	10		100		At 200° C. meters per sec.
Electron affinity ¹⁸	4.4					
Crystal system.....	Cubic	Cubic	Hexagonal	Cubic	Cubic	Volts
Structure type.....	Face-center cubic	Face-center cubic	Hexagonal close-packed	Face-center cubic	Face-center cubic	
Unit cell: ¹⁹						
a ₀	3.913	3.823	2.714	3.859	3.820	Hexagonal
c ₀			4.32		2.686	Hexagonal
					4.272	close packed

¹¹ Bur. of Stand., *Bull.* (1914).¹² Smithsonian Tables, 296.¹³ Smithsonian Tables, 296.¹⁴ Kaye and Laby Tables, 90.¹⁵ Grummach; *Ann. der Phys.* (1906).¹⁶ Holborn and Day.¹⁷ Crookes; *Proc. Roy. Soc.* (1891).¹⁸ Smithsonian Tables, 404.¹⁹ International Critical Tables, 340.¹ International Critical Tables, 4, 102.² Langmuir and Mackay; *Phys. Rev.*, 46, 377.³ Crookes; *Proc. Roy. Soc.* (1912).⁴ International Critical Tables, 1, 104.⁵ International Critical Tables, 1, 102.⁶ Fizeau.⁷ Gruneisen; *Ann. der Phys.* (1907).⁸ Kaye and Laby Tables, 27.⁹ Kaye and Laby Tables, 27.¹⁰ Hennig; *Zeitschr. Instrumentenkunde* (1910)

METALLOGRAPHY

The platinum metals, when alloyed with other members of the group, present to the metallographer very little of unusual interest, apart from the difficulty of examination. The metals are isomorphous and form solid solutions presumably of Roozeboom's Type 1. The difficulty of working at temperatures above 1600°C . prevents any determination of the liquidus or solidus with the apparatus at present available. The most general etching reagent is aqua regia, but this fails when the percentage of osmium, iridium, rhodium or ruthenium is high. In such cases heat etching or fusion with potassium bi-sulfate, or potassium hydroxide with 10 per cent. potassium nitrate, is sometimes useful. For palladium and palladium-rich alloys, a cold solution of aqua regia in some organic liquid (*e. g.*, alcohol, glycerin) or boiling concentrated nitric acid can be used.

Figs. 1 to 6⁴ show platinum and platinum with 5, 10, 15, 20 and 30 per cent. iridium. Platinum and platinum-5 per cent. iridium were etched in boiling aqua regia and the remainder were heat etched by heating in oxygen at 900 to 1000°C . It will be observed that the addition of iridium decreases the grain size but after 15 per cent. has been added, no further decrease takes place.

Figs. 9 to 12 show palladium and platinum with 10, 20 and 50 per cent. palladium. It will be seen that in this case the grain size becomes more uniform and smaller with additions of palladium to platinum, though not to the extent that occurs when iridium and platinum are alloyed. The 5 per cent. iridio-platinum and the palladium alloys are attacked very differently, in that some grains in the iridio-platinum seem to be much more rapidly attacked than others, while the attack in the case of palladio-platinum is equal in all the grains, concentrating at the boundaries. Rhodio-platinum is attacked in the same way as 5 per cent. iridio-platinum (Figs. 7 to 8).

SPECTROGRAPHY

Efforts have been made to make quantitative spectrum analysis with a Hilger quartz spectrograph,⁵ following the method outlined in Bureau of Standards Scientific Paper No. 444.

The quantitative estimations are based upon a comparison of the spectra of standard electrodes of known composition, with the spectrum of the material to be analyzed. Fig. 13 shows a spectrogram of numerous standard platinum-iridium alloys together with a platinum-iridium alloy of unknown composition. To obtain the best possible comparison, the unknown material is photographed between the spectrograms of each of the standard rods. The unknown material in this case was estimated to

⁴ Photomicrographs by C. S. Sivil, Baker & Co., Inc.

⁵ Experiments conducted by R. Rennie, Baker & Co., Inc.

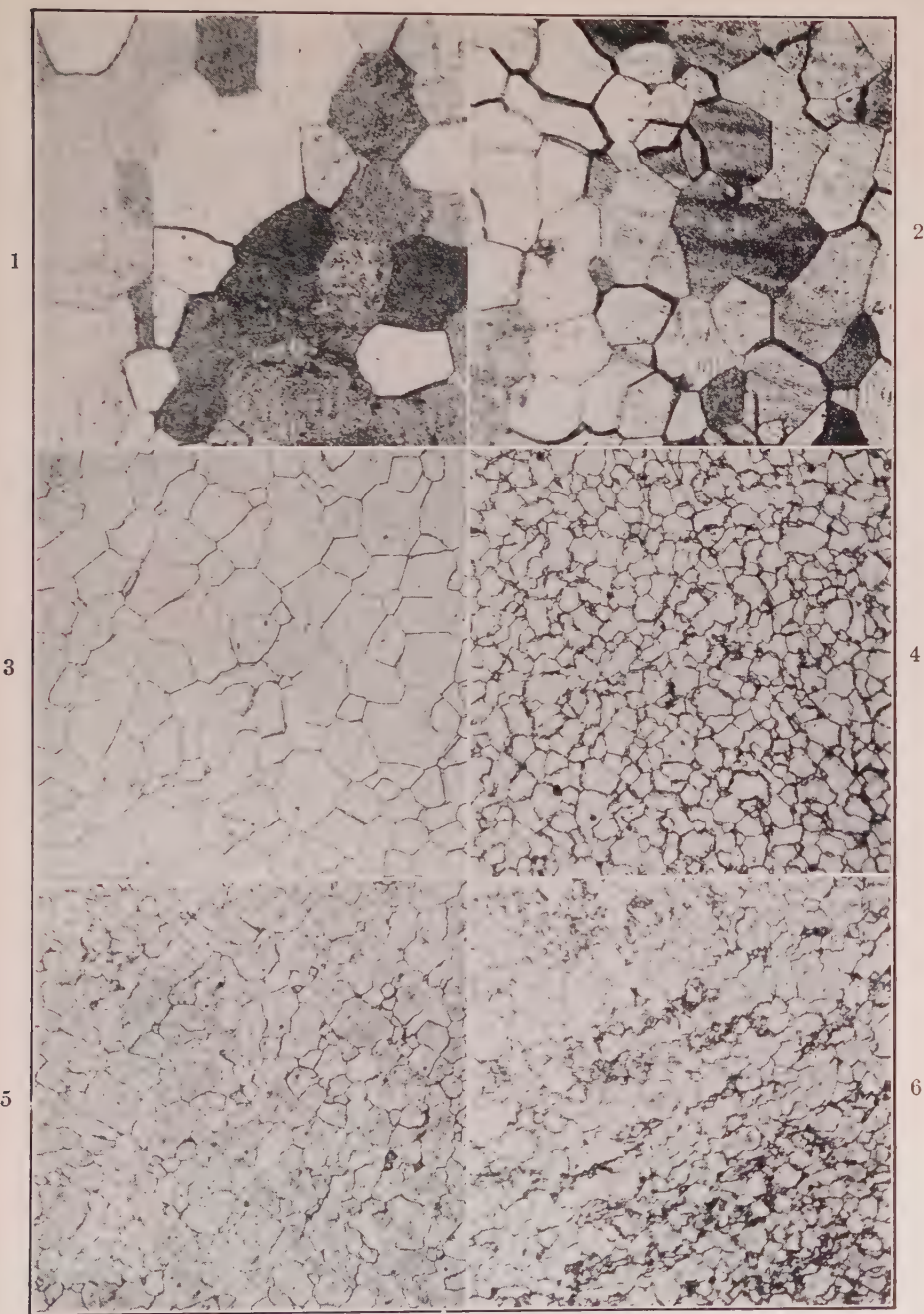


FIG. 1.—PLATINUM ANNEALED 1 HR. AT 1200° C. ETCHED WITH BOILING AQUA REGIA. $\times 100$.

FIG. 2.—Pt, 95; Ir, 5; ANNEALED 1 HR. AT 1200° C. ETCHED WITH BOILING AQUA REGIA. $\times 100$.

FIG. 3.—Pt, 90; Ir, 10; ANNEALED 1 HR. AT 1200° C. HEAT ETCHED. $\times 100$.

FIG. 4.—Pt, 85; Ir, 15; ANNEALED 1 HR. AT 1200° C. HEAT ETCHED. $\times 100$.

FIG. 5.—Pt, 80; Ir, 20; ANNEALED 1 HR. AT 1200° C. HEAT ETCHED. $\times 100$.

FIG. 6.—Pt, 70; Ir, 30; ANNEALED 1 HR. AT 1200° C. HEAT ETCHED. $\times 100$.

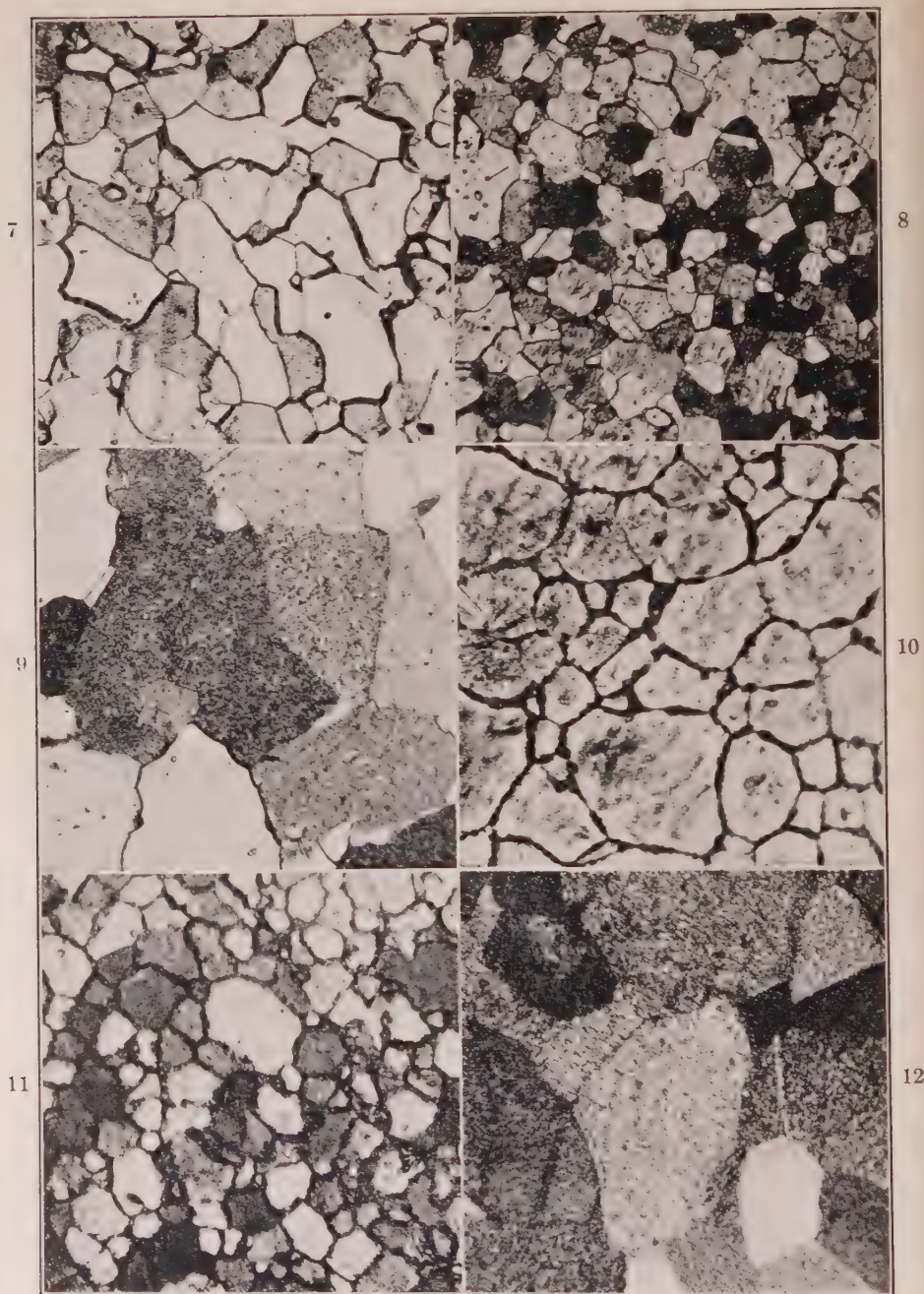


FIG. 7.—Pt, 90; Rh, 10; ANNEALED 1 HR. AT 1200°C . ETCHED WITH BOILING AQUA REGIA. $\times 100$.
 FIG. 8.—Pt, 80; Rh, 20; ANNEALED 1 HR. AT 1200°C . ETCHED WITH BOILING AQUA REGIA. $\times 100$.
 FIG. 9.—Pt, 90; Pd, 10; ANNEALED 30 MIN. AT 1200°C . ETCHED WITH COLD AQUA REGIA. $\times 100$.
 FIG. 10.—Pt, 80; Pd, 20; ANNEALED 30 MIN. 1200°C . ETCHED WITH COLD AQUA REGIA. $\times 100$.
 FIG. 11.—Pt, 50; Pd, 50; ANNEALED 30 MIN. 1200°C . ETCHED WITH COLD AQUA REGIA. $\times 100$.
 FIG. 12.—PALLADIUM; ANNEALED 30 MIN. AT 1200°C . ETCHED WITH BOILING HNO_3 . $\times 100$.

be somewhat short of 5 per cent. iridium and was later assayed to 4.26 per cent. iridium. The analysis of the alloys containing up to 15 per cent. iridium can be made with an accuracy of ± 1 per cent. iridium, and in less than 2 hr. Above 20 per cent. iridium, however, it is difficult to establish closer than ± 2 per cent.

Quantitative spectrum analysis of this kind is not of course a substitute for an exact assay, but it is valuable as a quick approximate estimation, especially as a chemical analysis of platinum metals is an expensive and tedious affair. For spectrum analysis of this kind, whole series of standard electrodes of Pt-Rh, Pt-Pd alloys, etc., are kept.

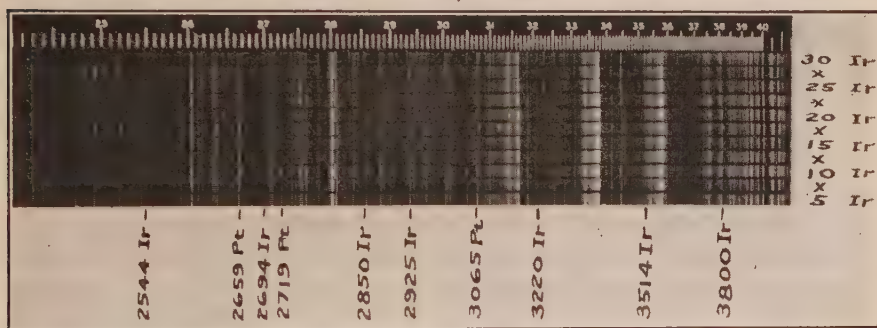


FIG. 13.—SPECTROGRAM SHOWING METHOD OF ESTIMATION OF COMPOSITION OF A PLATINUM-IRIDIUM ALLOY.

Spectrum analysis has the greatest value as a method of making semiquantitative determinations of impurities deleterious to the pure metal, chemical analysis of which might be impossible, owing to the minute quantity of the impurity. Thus, any platinum intended for use where exceptional purity is wanted, as for catalytic purposes, is spectrum-analyzed.

Spectrum analysis is also used to determine small amounts of impurities in returned platinum ware, thus establishing the cause of failure. To quote an example: a customer thought he had reason to complain about a shipment of platinum rings that had darkened. Spectrum analysis revealed silver, but the assay laboratory reported none. It was concluded that the silver was a surface contamination only, caused by the customer polishing the platinum after some silver soldering had been done on it. This proved to be the case.

ALLOYS

No attempt has been made to make a complete list of the binary alloys of the platinum group; a selection has been made of those which (1) have some commercial application, (2) are used in the separation of

the platinum metals in the chemical laboratory, (3) are encountered during the working of the metal. Practically the only previous systematic account of these alloys is that of Geibel,⁶ who gives some of the physical properties of the Pd-Au, Pd-Ag, Pd-Pt, Pt-Ir, Pt-Au, Pt-Ag series.

PLATINUM

Platinum-aluminum.—With less than 10 per cent. aluminum the alloys are white and malleable and not attacked by acids. The alloy containing 70.4 per cent. platinum corresponds to PtAl_3 , and is hard and brittle. Those with less than 9 per cent. platinum are soft, malleable and white. Above this the alloys are harder and yellow in color.

Platinum-calcium.—During melting, platinum may take up calcium, particularly under reducing conditions. The metal always shows calcium spectrographically, this being present probably both as platinum-calcium alloy and as CaO .

Platinum-carbon.—Carbon readily reacts with platinum, the metal freely taking it up even before reaching the melting point. On cooling the carbon settles out between the crystal grains, causing darkening and brittleness.

Platinum-cobalt.—Alloys are similar to platinum-nickel alloys but have a much higher electrical resistance. They are workable up to about 10 per cent. cobalt.

	Resistance, Ohms/Mil Ft.
Pt 97.5, Co 2.5.....	170
Pt 95, Co 5.....	245
Pt 90, Co 10.....	255

Platinum-copper. These two metals form complete solid solutions. Up to 10 per cent. copper the alloys do not blacken on heating, but above this the alloys do blacken and become increasingly difficult to work. They may be hot rolled up to about 30 per cent. copper and above that they are hard and brittle. The addition of copper to platinum increases the electrical resistance to a most unexpected extent, and an alloy like 80 platinum-20 copper should be useful as a stable non-oxidizing, resistance

⁶ W. Geibel: Über einige elektrische und mechanische Eigenschaften von Edelmetall Legierungen.—I. *Zeitschr. anorg. Chem.* (1910) **69**, 38; Pt. II, (1911) **70**, 240.

alloy. The following table gives some electrical properties of the platinum-copper alloys:

	Resistance, Ohms/Mil Ft.	Temperature Coefficient of R per °C.	Electromotive Force against Pt at 1100° C.
Pt 95, Cu 5.....	227	0.00015	+3.48
Pt 90, Cu 10.....	335		+5.05
Pt 85, Cu 15.....	430		
Pt 80, Cu 20.....	540	0.00016	+0.80
Pt 75, Cu 25.....	530	0.00012	
Pt 70, Cu 30.....	500		-5.05

Nitric acid does not attack the alloys containing more than 50 per cent. platinum.

Platinum-gold.—These are complete solid solutions. Addition of gold rapidly hardens platinum, and the limit of workability is reached at about 10 per cent. gold. The alloys with the gold in excess work satisfactorily; it is, however, difficult to get them quite homogeneous, as would be expected from the form of the liquidus and solidus. Some of the physical properties of the alloys are given in the following table:

	Brinell Hardness		Erichsen Test, Mm.	Resistance, Ohms/Mil Ft.
	Hard	Annealed		
Pt 95, Au 5.....	177	98		133
Pt 90, Au 10.....	222	162		
Pt 40, Au 60.....	226	174	6.9	156
Pt 30, Au 70.....	193	135	9.7	153
Pt 20, Au 80.....	158	104	11.3	122
Pt 10, Au 90.....	105	61	12.2	70

Platinum-iridium.—This series of alloys is the most important of all platinum alloys. In chemical ware, in electric work, and in jewelry, pure platinum is too soft for use so it is generally hardened by the addition of iridium in varying amounts. For example, in jewelry "medium hard" platinum contains 5 per cent. iridium and "hard" platinum contains 10 per cent. iridium. The limit of workability is 30 to 35 per cent. iridium. The alloys are solid solutions which usually show a slight amount of coring in the crystal grains, but this inhomogeneity can be removed by long annealing. A few physical properties are given in the following table:

	Brinell Hardness		Erichsen Test			Electrical Resistance Ohms/ Mil Ft.
	Hard	Annealed	Hard, Mm.	Annealed 1100° C., Mm.	Annealed 1200° C., Mm.	
Pt 100.....	97	47	7.8	12.2	12.2	60
Pt 95, Ir 5.....	170	110	7.1	10.7	10.7	120
Pt 90, Ir 10.....	220	150	7.1	10.0	10.4	160
Pt 85, Ir 15.....	280	190	7.0	9.7	10.2	185
Pt 80, Ir 20.....	330	230	7.0	9.0	9.7	200
Pt 75, Ir 25.....	370	270	4.1	8.0	7.8	210
Pt 70, Ir 30.....	400	310			2.0	210

The Erichsen figures are interesting in that they afford further evidence that with increasing iridium content higher annealing temperatures are required; the increase in ductility of the material annealed at 1200° C. over that annealed at 1100° C. is 0.0 mm. for platinum, 0.0 for the 5 per cent. alloy, 0.4 for the 10 per cent., 0.5 for the 15 per cent., and 0.7 for the 20 per cent.; this means of course that 1100° C. is sufficient for the first two and increasingly insufficient for the others. The figures also indicate that a short time at 1200° C. is not sufficient for the 25 and 30 per cent. alloys. It is also of interest that in the hard-worked condition the ductilities are not markedly different in the various iridio-platinum alloys, until more than 20 per cent. is added, when the ductility rapidly decreases.

On heating the alloys the surface darkens considerably within the range 900 to 1100° C., probably due to the formation of iridium oxide. On heating to higher temperatures the oxide decomposes and the surface regains its white appearance. This oxide formation is generally observed only when the heating is done in an electric furnace. It may be mentioned that metallic iridium becomes heavily coated, under similar conditions, with a blue-black oxide. Above 900° C. iridium-platinum alloys begin to lose weight somewhat, due to the volatilization of the oxide. This property prevents the use of high percentages of iridium in crucible ware where constancy of weight is essential. It also explains why the use of platinum-10 per cent. iridium has been discontinued for thermo-couple work, since the electromotive force is not constant.

Platinum-iron.—Iron alloys rapidly with platinum to form solid solutions and it is therefore very necessary in annealing operations to keep iron out of contact with platinum. Also, in the ordinary operations of rolling, wire drawing, etc., iron may become imbedded in the surface of the platinum and then on subsequent heating be easily dissolved into the latter. Where pure platinum is required the metal must always be treated before reheating with hot concentrated hydrochloric acid to

remove any adhering iron particles. Foreign iron may also be removed by treating the surface with borax and heating for several hours.

Platinum-lead.—Low fusing alloys are readily formed, as many a chemist knows to his sorrow when the bottom of a platinum crucible melts through.

Platinum-magnesium.—Platinum may take up magnesium to the extent of 3 per cent., and indeed spectroscopic amounts of magnesium are generally to be found even in high grade platinum.

Platinum-mercury.—Under ordinary conditions platinum does not amalgamate directly with mercury, but on heating to about 200° C., “wetting” does take place. Also, if a current is passing between the platinum and the mercury an alloy may be formed. Sodium amalgam reacts with platinum and a process for removing platinum from its crushed ore has been developed by Zachert which depends on this property.

Platinum-nickel.—These two metals form useful alloys which are probably solid solutions. The alloy containing 5 per cent. nickel has become of importance due to its wide use in radio tubes as the heating filament. The resistance of the 5 per cent. alloy is 140, and of the 10 per cent. alloy is 180 ohms/mil ft.; the temperature coefficient, 0–1200° C., is 0.00189 per °C. for the 5 per cent. alloy.

Platinum-osmium.—Osmium has about 2½ times the hardening effect of iridium on platinum, and also increases the electrical resistance 2½ times as quickly. It is very difficult to work an alloy containing more than 10 per cent. osmium, owing to the great hardness and lack of ductility. Care has to be taken to anneal under reducing conditions, as otherwise osmium burns off.

Platinum-palladium.—Palladium does not harden platinum to the same extent as do the other metals of the group, and the whole series of alloys, which are perfectly homogeneous solid solutions, is easily workable. The alloy of maximum hardness is that containing about 25 per cent. palladium. Some figures for Brinell hardness and electrical resistance are given in the following table:

	Brinell Hardness		Erichsen Test, Mm.	Resistance, Ohms/Mil Ft.
	Hard	Annealed		
Pt 90, Pd 10.....	160	85	11.1	130
Pt 80, Pd 20.....	170	95	11.5	160
Pt 75, Pd 25.....	175	100	8.1	170
Pt 50, Pd 50.....	165	90	7.9	180
Pt 25, Pd 75.....	155	80	9.5	145

Platinum-rich alloys have the chemical properties of platinum rather than of palladium. For example, boiling nitric acid has no solvent

action on alloys containing up to 25 per cent. palladium, nor do alloys with up to the same amount show any of the color effects of palladium on heating.

Platinum-rhodium.—Platinum and rhodium form solid-solution alloys. They are workable up to about 50 per cent. rhodium although only with difficulty in the higher percentages. The rhodium does not harden platinum as much as iridium, osmium and ruthenium, but hardens it more than does palladium. Some physical properties are given in the following table:

	Brinell Hardness			Tensile Strength, Kg./Mm ² .	Resistance, Ohms, Mil Ft.	Temperature Coefficient per °C., 0-1200° C.
	Hard	Annealed				
		1000° C.	1200° C.			
Pt 96.5, Rh 3.5.....	107		65	48	103	0.00195
Pt 90, Rh 10.....	165		90	72	110	0.00135
Pt 80, Rh 20.....	211	169	107	108	125	0.00120
Pt 50, Rh 50.....	323	254	138		134	

Platinum-rhodium alloys have a lower rate of volatilization than has platinum and do not crystallize so readily. They have therefore been used to some extent in crucible ware. One preferred alloy for this purpose is that containing 3½ per cent. rhodium. These valuable properties also lead to their use as a positive element in precious metal thermocouples. The e. m. f. against platinum is not so great as that of the corresponding platinum-iridium alloy, but their constancy has caused them to replace the latter almost wholly for thermocouple work.

Platinum-ruthenium.—Alloys of platinum and ruthenium are somewhat similar to platinum-osmium alloys, ruthenium having about the same hardening effect on the platinum as osmium. The Brinell hardness of the annealed 10 per cent. alloy is 210 and its electrical resistance is 245 ohms/mil ft. The alloys lose considerably in weight on heating due to volatilization of the added element, although to a lesser extent than in the case of platinum-osmium. The limit of workability is about 10 to 15 per cent. ruthenium.

Platinum-silicon.—Silicon in the elementary state reacts with platinum to form brittle alloys. It has been shown that silica in the presence of carbonaceous material or of hydrogen will have the same effect. When a platinum crucible, which has been used for silica determination, shows a brilliant crystalline structure on the bottom and probably develops a crack, it is fairly certain that carbonaceous material has been

present with the silica, or a reducing flame, allowing hydrogen to pass through platinum to the silica, has been used in heating the crucible.

Platinum-silver.—The addition of silver to platinum causes rapid hardening. The alloys with excess of silver, such as are used in dentistry, electrical contacts, etc., are hard but fairly ductile. The platinum, even in proportions of a few per cent., seems to reduce the rate of tarnishing of the silver. The alloys of this series are not continuous solid solutions as in the case of platinum-gold and palladium silver, and there exists possibly a compound of formula PtAg_2 . The metals do not mutually dissolve readily and tend to separate on cooling.

IRIDIUM

Other than the platinum-iridium alloys already described, iridium alloys have not a great importance.

Iridium-osmium.—The naturally occurring alloys, called iridosmine or osmiridium, are very hard and are used on pen points. The manufactured alloys find considerable use in special ignition work on account of their extremely high fusing points and their hardness.

Iridium-phosphorus.—These alloys are historically interesting as being the product of the Holland process for obtaining a synthetic alloy to replace the natural osmiridium grains on pen points. The alloy is obtained by adding white phosphorus to iridium or osmiridium at a very high temperature, casting into sheets and breaking up to the desired size.

OSMIUM

Osmium alloys are of very little importance except in combination with iridium. At the present time synthetic alloys high in osmium are made for pen point material, and for "sparking point" alloys.

PALLADIUM

Palladium forms a number of useful alloys and easily ranks second in importance in the platinum family.

Palladium-copper.—Palladium and copper form a complete series of solid solutions which melt intermediately between the melting points of the constituent metals. They are malleable and ductile. The electrical resistances are lower than those of the corresponding platinum alloys. For example, 70 palladium-30 copper = 285 ohms/mil ft., 80 palladium-20 copper = 270 ohms/mil ft.

Palladium-gold.—These form solid solutions and give a much better series of alloys than in the case of platinum-gold. There is no tendency to segregate, the liquidus and solidus lying very close together. Addition of palladium to gold rapidly raises the melting point, the increase being

greater than when the corresponding weight of platinum is added to gold. The alloys, due to their high melting point, non-oxidizability, and chemical stability, have found a certain use in laboratory ware under the trade name of "Palau," "Rhotanium," etc. Sometimes some platinum is added to give hardness; "Palorium" is such an alloy. The early "white golds" used in jewelry were gold-palladium alloys but these have been mostly replaced by gold-nickel alloys which are whiter and harder. Some physical properties are given in the following table:

	Brinell Hardness		Erichsen Test, Mm.	Resistance Ohms/Mil Ft.
	Hard	Annealed		
Pd 90, Au 10.....	124	95	10.9	99
Pd 80, Au 20.....	135	100	9.7	113
Pd 70, Au 30.....	180	128	11.3	145
Pd 60, Au 40.....	192	118	11.2	161
Pd 50, Au 50.....	186	98	12.0	176
Pd 40, Au 60.....	190	101	8.8	165
Pd 30, Au 70.....	175	96	11.2	113
Pd 20, Au 80.....	165	94	10.6	109
Pd 10, Au 90.....	120	70	11.2	67

Palladium-iridium.—Iridium does not harden palladium to the same extent that it does platinum.

	Brinell Hardness		Resistance, Ohms/Mil Ft.
	Hard	Annealed	
Pd 95, Ir 5.....	107	62	86
Pd 80, Ir 10.....	130	81	123
Pd 85, Ir 15.....		110	210
Pd 80, Ir 20.....		152	235

Above 20 per cent. iridium the alloys are workable only with great difficulty.

Palladium-nickel.—These are solid solutions showing a minimum of 1265° C. at 50 per cent. palladium.

	Brinell Hardness, Annealed	Resistance, Ohms/Mil Ft.
Pd 90, Ni 10.....	163	145
Pd 80, Ni 20.....	198	138

Above this amount of nickel the alloys are not workable.

Palladium-osmium.—Owing to the difficulty of controlling the composition of these alloys, little has been done with them. The alloy with 75 palladium, 25 osmium shows a hardness of 200 hard

worked and 160 annealed, and has a resistance of 120 ohms per mil ft.

Palladium-rhodium.—Palladium and rhodium form apparently a series of solid solutions.

	Brinell Hardness		Resistance, Ohms/Mil Ft.
	Hard	Annealed	
Pd 95, Rh 5.....	134	72	126
Pd 90, Rh 10.....	147	79	155
Pd 85, Rh 15.....	195	104	

The 50-50 alloy is friable and quite unworkable.

Palladium-ruthenium.—Palladium and ruthenium form apparently a similar series of alloys, except that above 10 per cent. the alloys are too hard to work.

	Brinell Hardness	
	Hard	Annealed
Pd 95, Ru 5.....	152	92
Pd 92.5, Ru 7.5.....	230	130

Palladium-silicon.—Compounds SiPd₂ and SiPd are formed. Owing to the ease with which the silicide is formed palladium cannot be melted without embrittlement in a siliceous crucible.

Palladium-silver.—These form a complete series of solid solutions. A table of some of the physical properties is given below.

	Brinell Hardness		Erichsen, Mm.
	Hard	Annealed	
Pd 90, Ag 10.....	130	74	6.5
Pd 80, Ag 20.....	294	248	8.0
Pd 70, Ag 30.....	282	190	8.7
Pd 60, Ag 40.....	248	122	9.1
Pd 50, Ag 50.....	169	104	10.0
Pd 40, Ag 60.....	130	88	10.8
Pd 30, Ag 70.....	126	72	11.0
Pd 20, Ag 80.....	114	59	11.4
Pd 10, Ag 90.....	95	53	11.7

RHODIUM

The only important series of alloys of rhodium is that of platinum-rhodium which has already been described.

RUTHENIUM

Ruthenium is scarce and its alloys are unimportant. It is used to some extent for hardening palladium and platinum and seems to act generally very similarly to osmium.

TERNARY AND QUATERNARY ALLOYS

It is impossible even to enumerate the many ternary and quaternary alloys containing the platinum metals. In a general way the platinum metal additions are made (1) to raise the melting point, (2) to decrease the rate of oxidation, (3) to increase the hardness. Although a great many complex alloys containing platinum metals are put to a variety of uses, the thermal diagrams, except in one or two cases, have not been worked out. It will therefore be best not to attempt any consecutive listing of these alloys but to leave mention of the alloys to the next section.

USES

Laboratory Ware.—Everyone knows the importance of platinum in the laboratory and realizes that without it he would be at a tremendous disadvantage in analytical and other work. Platinum has no equal for laboratory ware, and although it may be more expensive initially than certain substitutes, it actually is cheaper because the scrap value is so high and because it may be used under so many different conditions. It should be emphasized however that platinum vessels are not foolproof and should be properly cared for; when making fusions, for example, it is well to give thought to what chemical changes go on during the reaction, and see that no low melting metals are produced by the fusion. A platinum crucible should be heated to no higher a temperature than is necessary because it will crystallize and the higher the temperature the greater is the size of the crystal grain; neither should it be heated any longer than is necessary. The most important fact to remember is that oxidizing conditions should be maintained throughout the heating; if the crucible bottom is in the inner cone, *i. e.*, reducing zone, of the flame, the hydrogen simply passes through the platinum, reduces various oxides to the element which then reacts with the platinum. Similarly, if platinum crucibles are heated in gas or electrically-heated muffles, oxidizing conditions should be maintained in the muffle; also it is preferable to keep the crucible away from the siliceous bed. Platinum crucibles should not be roughly handled; if distorted they can easily be reshaped, but every time this has to be done shortens the life. A platinum crucible is a compromise; the pure metal is excellent from the constancy in weight point of view, but it is very soft; additions of iridium or rhodium

stiffen it up and lower the rate of crystallization. Iridium unfortunately is so volatile that the crucible loses weight on heating so the percentage should be kept to 0.3 per cent. or less. Rhodium does not volatilize to the same extent and for this reason is a preferable addition.

Chemical Industry.—Platinum apparatus was formerly used in industry on quite a large scale; sulfuric acid was concentrated in platinum vessels, condensing worms of considerable size were used, but the great expense has put them in the discard almost completely. More and more, chemical industry is becoming the industry of catalysis and since the platinum metals are generally such active catalysts, we find that platinum and the other metals of the group are being increasingly used as catalysts. It is well known that platinum is used in the sulfuric acid contact process, but it is perhaps not so well known to what an extent it is being used in the chamber sulfuric acid process and in the nitric acid industry; of course, in both of these the platinum is used as the catalyst, in the form of gauze, in bringing about the reaction of NH_3 and air to form nitrous gases. Modern developments in synthetic organic chemistry are opening up large new fields in industry and the platinum metals in their capacity as catalysts are becoming increasingly important. In the electrochemical industry considerable quantities of platinum are still used as electrodes, although in many cases substitutes have been found. The alloys 90 platinum-10 rhodium and 87 platinum-13 rhodium are used as thermocouples to indicate temperatures of furnaces, etc.; platinum is used as lining for bomb calorimeters, as electrodes, furnace windings, filter cones, tips for crucible tongs, tweezers, etc., in the laboratory.

Electrical Industry.—Though electrical contacts are easily overlooked, due to their insignificant size, they are still of great importance in the functioning of the machine and in most cases are actually the most vital part thereof. Without a perfect make and break of current no combustion motor could work properly and no thermostat could be dependable.

Fine silver, silver alloys, and tungsten are all used in tremendous quantities for contact work, but platinum alloy points are generally used under severe conditions and wherever absolute dependability is needed. Take for example, the magneto. In a magneto only a very limited number of metals or alloys are of any use, because:

1. The mechanical strain is great, as the impact, many times a second, must be considerable; thus only a very hard and tough metal can resist without flattening out or crumbling up.

2. As a good contact must be assured even after long operation in moist air, which may contain acids in industrial centers, only very noble metals are dependable.

3. The break gap must be small on account of the limited space and the speed of making and breaking; this requires a contact metal of low vapor pressure.

These conditions eliminate all soft or fragile or base metals and alloys. Of the noble metals, silver and gold cannot be used on account of their comparatively low evaporation points; the vaporized metal prolongs the arc and lowers the effect of the break of contact. Only platinum and alloys of the platinum group give good and efficient service as they fulfill the above requirements in a remarkable way. It has been found that among the great variety of platinum alloys 80 platinum-20 per cent. iridium gives the best results. The contacts remain smooth without any oxidation; there is no flattening out or crumbling of the metal, and the high evaporation point cuts the spark short, giving best results in electrical high tension effect.

Though tungsten has been applied on account of its high melting point, great hardness and toughness, its resistance to oxidation under the electrical sparking effect is low. This causes a considerable increase in contact resistance and may cause difficulties, especially in starting the motor.

Palladium-silver alloys, particularly the 60 palladium-40 silver, have shown usefulness as contacts; the alloys are hard, non-tarnishing, and possess a fairly high melting point.

Where extremely severe conditions are encountered, "sparking point" alloys are used. These are made wholly of platinum metals and are extremely hard, so much so that they are quite unworkable and have to be ground to the proper shape. They are naturally much more expensive than the ordinary contact point.

Jewelry.—Fifty-seven per cent. of the platinum used goes into jewelry. The manufacturer likes it because it is strong, ductile, malleable, and the customer likes it because it holds diamonds, etc., very securely and because it is sufficiently expensive.

As previously mentioned, platinum containing 5 and 10 per cent. iridium is generally used; sometimes also palladium, rhodium or ruthenium may be used as the alloying element. Up until very recently articles could be stamped platinum if they contained 95 per cent. of the platinum metals; however, when palladium dropped in price below platinum and since it has only about one-half the specific gravity of platinum, articles of very different intrinsic values could be stamped "platinum." This was unjust, so laws have been recently passed by which articles marked "platinum" must contain 95 per cent. pure platinum. Palladium has found considerable use as a jewelry metal; it is generally hardened sufficiently by small amounts of platinum metals. It is non-tarnishing and to the wearer is quite indistinguishable from platinum.

Electroplating.—There are quite appreciable quantities of platinum used in electroplating; there are good solutions on the market, generally phosphates, which give bright non-tarnishing finishes. They are used in jewelry and in fine instruments, or wherever non-tarnishability is required.

A good palladium plating solution has been developed; the solution has an excellent throwing power, and, since the plate is white and non-tarnishing, may find quite wide application. Rhodium plating baths are also in use and are particularly brilliant, due to the high reflecting power of rhodium.

Photography.—When the price of platinum was lower, salts of the metal found a very large use in photographic work, but this has to a great extent been discontinued owing to the cost; this is unfortunate since platino-type photographs are desirable both for beauty and lasting qualities. Also the use of barium platinocyanide in X-ray fluorescent screens has been superseded by calcium tungstate.

Penpoints.—The tips of pens must be very hard, non-oxidizing at ordinary temperatures and resistant to acids which may be present in the ink; iridium-tipped pens are generally used today but these actually are osmiridium alloy. For many years native Tasmanian osmiridium grains have been and are used, but synthetic osmium alloys which have been given the suitable crystal structure by special treatment are now replacing the natural alloy to a very considerable degree.

Radio.—A considerable amount of platinum is used as the heating filament in radio tubes, the alloys generally used being 90 platinum-10 iridium or 95 platinum-5 nickel. The former is perhaps somewhat more dependable as regards uniformity, but the slightly lower cost of the latter has led to its very wide application.

Explosives.—In the explosives industry 90 platinum-10 iridium and 80 platinum-20 iridium are used as fuse wires; the uniformity of resistance and permanence cause these alloys to be preferred to all other materials since dependability is of great importance.

Rayon.—In the manufacture of rayon the liquid is squirted through small holes and then allowed to solidify. These holes, about 0.004 in. dia., are made in the base of a metallic cup or spinneret and are usually below 100 per cup in number. Spinnerets are generally made of precious metal alloys because it is essential that metallic impurities be not present in the rayon, and such might easily be introduced by the action of acids in the solution on the cup material. Furthermore, as it is necessary to clean out the holes which become stopped up, it is preferable to be able to use acids for this purpose, and to know that the metal will be unattacked during the operation. Some platinum cups are used but more generally gold containing up to 30 per cent. platinum or palladium is the preferred material.

Medicine.—The medical profession uses 80 platinum-20 iridium, 75 platinum-25 iridium, and 70 platinum-30 iridium, for hypodermic needles and platinum for cautery tips. Platinum and palladium tubes are used for regulating the "hardness" of X-ray tubes, their use being dependent on their permeability to hydrogen on heating. Osmic acid is

a most valuable agent in microscopy as a staining and preserving fluid. Its use depends upon the fact that this compound is readily reduced by almost all organic substances, especially by the fats and oils. In this reduction there is deposited either a lower oxide, or perhaps metallic osmium, which causes the tissue to become evenly dark bluish black without losing its transparency or presenting any granular precipitation. The tissues, if fresh when immersed, retain their texture as in life, and resist decomposition. The rapidity with which different tissues are stained varies, which is a very great advantage. The same property causes it to be used in the Mitchell system of recording finger prints which has become more or less standard throughout the world.

Dentistry.—The dentist uses a host of alloys containing platinum and palladium in various proportions. Probably chief of these are the alloys of platinum, palladium and gold used for pins or anchorages for artificial teeth. Nearly all good dental work now contains alloys to which certain necessary properties are given by the addition of palladium and platinum, chief of these being high melting point (quite necessary in constructing the restoration), and elasticity or springiness, essential on certain types of bridgework. High grade orthodontia demands alloys containing platinum and palladium. The dental precious metal alloys are generally quite complicated, often consisting of as many as six metals, gold generally predominating. Platinum foil is more and more being used, this for making of so-called porcelain jacket crowns and taking the shape of tooth cavities.

Dyeing.—Certain ruthenium salts are used in the dye industry; for example, one ruthenium ammonium base can be used for dyeing silk or wool purple without a mordant. There is also a ruthenium containing "Prussian purple" which gives a brilliant purple dye, fast to acids.

DISCUSSION

E. A. CAPILLON, New York, N. Y.—Why is a platinum alloy used in connection with the spinneret cups? As I understand it, the solution used is only about 15 per cent. sulfuric acid. Why could not some other acid-resisting alloy be used which would be cheaper?

E. WICHERS.—The discussion on gases in these metals interested me especially. It ought now to be possible by the use of the Ajax furnace, to melt in high vacuum and actually find the difference in properties between these metals melted in air and melted in vacuum. Are the physical properties in the table, the ones that have no footnote references, your own determination, Dr. Carter?

F. E. CARTER.—The majority of them.

E. WICHERS. May I add just an observation on the mercury-platinum amalgam? Dr. Carter says that no amalgamation takes place at ordinary temperature, which I think is a general observation. Some time ago, we immersed a piece of platinum foil in mercury for three months at room temperature. At the end of that time

distinct amalgamation of the platinum had occurred, although the foil was still intact and not a very large amount of mercury had been taken up.

H. T. REEVE, New York, N. Y.—In connection with the hot working of platinum, and the ease with which platinum and iron form alloys, we have found surface contamination to occur during cold rolling which can be removed by boiling in hydrochloric acid. Would not hot rolling cause certainly more than surface contamination, probably alloying?

On page 763 the term "vacuum-poured" occurs. I believe we would all be very interested in hearing if Dr. Carter has worked out some system of pouring metal in vacuum.

On page 770, does the reaction with carbon mean that it would be dangerous to cast platinum in a graphite mold, and if so, are molds of other materials available?

In regard to the platinum-copper alloys, the melting point of the 80-20 alloy is indicated in the International Critical Tables as around 1550° C. If this is correct, the alloy shows promise for furnace windings because of its high resistance. Therefore, any further information as to the life of such a winding at temperatures beyond which nichrome is not available would be valuable. It would seem that the melting of such an alloy in the air offers somewhat of a problem from the standpoint of the container, as cuprous oxide is very active in attacking most kinds of crucibles and graphite probably cannot be used.

Finally, in regard to the data on iridium alloys, is it a fact that a high-iridium alloy will not oxidize if kept continuously above 1100° C.? It is well known that ordinary commercial platinum deposits crystals of the metal near the turns of a furnace winding, presumably due to alternate oxidation and decomposition of the oxide.

E. M. WISE, Bayonne, N. J.—I would like to ask Dr. Carter for a little further information on platinum and palladium plating, particularly in regard to the thickness required. In my own experience no difficulty was noted in producing thin, lustrous deposits, but these did not afford complete protection. In some later experiments heavy deposits of palladium were produced which afforded complete protection against tarnishing. This should be useful in producing stainless sterling silver.

I believe that the use of electroplates of adequate thickness should be emphasized. If platinum or palladium plate is used it must be thick enough to be continuous, not merely enough to color the article.

I would like to ask Dr. Carter whether the hardening effect of iridium on platinum is due merely to solid-solution hardening or possibly to some other phenomenon.

The high electrical resistance shown by the platinum-copper alloys, together with certain phenomena observed in alloys containing platinum and copper, would strongly suggest the presence of a new phase existing over some small range of composition, thus presenting a close analogy to the palladium-copper system.

Any information available regarding the resistance-temperature relation for the 50 atomic per cent. copper-platinum alloy would be of interest.

I would be glad to have some information regarding the properties of the palladium content dental alloy known as Palladent.

F. E. CARTER.—About the platinum alloy spinnerets, I think I practically answered that in the paper. The precious metal alloys are used since it is essential that metallic impurities be not present in the rayon and these might easily be introduced by the action of acids in the solution on the cup material. I think possibly, from what I know of the subject, the more important point is that when it is necessary to clean out the holes which become stopped up, heating is very often resorted to. It is better therefore to use something which will not oxidize.

Referring to the Ajax furnace for vacuum work: In the discussion of a paper by Brace and Ziegler, that question was brought up by Dr. Jordan.⁷ He pointed out the difficulty of finding a suitable container for determination of the gases in metals, in that at high temperatures, particularly with the platinum metals, you get reactions between the metal and the refractories. This occurs at temperatures of 2000° and 2500° C. at which temperatures we really do not know much about chemical reactions. Under these conditions, some peculiar reversible reactions take place; *e.g.*, calcium is taken out of lime by platinum, when you are working in a vacuum, and that is one difficulty in studying the platinum metals in the absolutely gas-free states.

I only introduced the reference to mercury amalgam in the paper as a result of a problem I encountered many years ago. A concern put out a thermometer with an automatic cut-out, the mercury climbing up a platinum wire and cutting off the current. There was continual trouble due to action between the platinum and the mercury. I found that it did not take place until a temperature of 200° C. was attained, and the statement in the paper is simply based on those few experiments. I still believe that for practical purposes there need be no worry about platinum forming an amalgam until that temperature is attained.

As to hot working, there is of course a certain amount of alloying going on at the surface, but after hot rolling a good cut must be taken on both sides of the platinum bar. It does not seem to alloy right through the platinum at the temperature at which the hot rolling is done. If platinum is put in a furnace at 1500° C. and there is the slightest bit of iron in that furnace, there will be a thorough alloying very quickly, but at the temperature used for hot rolling, it apparently does not go more than just slightly below the surface.

As mentioned in the paper, the reference to vacuum-pouring is academic rather than practical, but I know that Krupp puts out a small furnace for handling reasonably large quantities of metal where actually melting and pouring are accomplished a vacuum. I should think that it would be very useful for people who wish to work with metals absolutely gas-free. I do not know that the Krupp company recommends this furnace for platinum, but certainly for some of the nickel alloys it is being used.

For casting platinum, graphite slabs are often used. It does not seem to contaminate the platinum seriously, but I believe that for chemically pure platinum graphite slabs should not be used.

We did not regard the platinum-copper resistance alloys as a heating element because the temperature coefficient is very small. If pure platinum is heated to 1500° C., it has practically the same resistance as platinum-copper alloys. I have not calculated this, but knowing that at 1300° or 1400° C. platinum has the same resistance as the 90 per cent. platinum 10 per cent. iridium alloy, and here where you have a smaller temperature coefficient the value of the alloys for high-temperature work is still less. We were thinking more of standard resistances. We think there is a demand, or should be a demand, for non-tarnishing and very constant precious metal resistance wires for standard resistances, for work at ordinary temperatures.

It is my belief that if you keep platinum-iridium alloys above 1100° C., oxidation will not occur. You will not get a tarnished surface because the iridium oxide decomposes. It forms at about 900° and decomposes at about 1100° or 1200° C. If iridium-platinum is heated above that temperature, the bright metal will be obtained again. It does not prevent the volatilization of either the iridium or the platinum above that temperature, and the iridium will oxidize as the temperature falls; *i. e.*, it will get into the stable range of the iridium oxide.

We have been making and selling for many years platinum and palladium plating solutions, particularly platinum. We have put plates on as heavy as 0.010 in., but

⁷ See page 564.

we supply different solutions for a flash plate or a heavy plate just as the customer may desire. They last very well indeed; even what we call the flash plate will stand a very considerable amount of wear before the metal underneath is exposed. We guarantee what we call the medium plate or the heavy plate.

E. M. WISE.—What would you consider a flash plate and a medium plate?

F. E. CARTER.—One ten-thousandths of an inch is a fairly good plate.

E. M. WISE.—That would be satisfactory, but one of these simply colored plates is quite unsatisfactory.

F. E. CARTER.—Oh, yes.

E. M. WISE.—There are a lot of those.

F. E. CARTER.—If an object is just held over a platinum bath, not much can be expected. As regards the hardening effect of iridium, as far as we know, the alloys of platinum and iridium are purely solid solutions. We find that as far up as one can go, and still have a real workable alloy, which is 30 or 35 per cent., the hardness increases and tends to become constant around 30 or 40 per cent. We know that an alloy of iridium with a few per cent. of platinum in it is very hard, but not as hard probably as alloys in the middle of the curve. Pure iridium is quite workable, but with the slightest amount of other platinum metals present, it is difficult to work at all. It must be worked at a very high temperature, too. You mentioned 50-50 platinum-copper.

E. M. WISE.—Fifty-fifty atomic.

F. E. CARTER.—Say 80 platinum, 20 copper by weight. That comes within our range, of course. It is workable and it oxidizes with quite a black film. They are alloys which work fairly well, provided they are worked hot.

Palladent is an alloy of palladium and silver containing 40 per cent. palladium.

S. J. BALUT, New York, N. Y.—Dr. Carter, will you discuss the segregation of platinum alloys, particularly iridium-platinum and platinum-palladium? I mean in fairly large melts of 50 or 100-oz. bars.

F. E. CARTER.—You do not mean the coring of the crystal grains. You mean probably the segregation at the top and the bottom of the bar. We have never noticed anything of that kind. If you pour at the right temperature and chill at the right temperature, there is really no difference in one part of the bar from another. That is absolutely sure, because if you take an 80 per cent. platinum 20 per cent. iridium alloy (used so much in fuse wires where the resistance has to be very constant), each part of the bar has the same resistance as the other, and we use that as a careful check. We have practically never found, if we get the proper mixing, that there is segregation of any sort. Platinum-palladium alloys are equally free of segregation.

Gold, Silver, Copper Alloys

BY FREDERIC E. CARTER,* NEWARK, N. J.

(New York Meeting, February, 1928)

THE gold, silver, copper alloys have been the subject of several fairly complete investigations by Jänecke, Sterner-Rainer¹ and others, and indeed it would seem as if almost too much labor had been expended on them when one thinks of the numerous other ternary alloys calling for more light; however, the combinations of the three metals are actually so widely used in jewelry that they merit perhaps the work done on them. There are a few properties of importance and interest not treated by the authors mentioned which the writer investigated some little time ago, and therefore he has ventured to put on record the results of some of his tests made at that time. He has chosen, as being the two series of most importance to the jeweler, only the 14 and 18-kt. golds, so the subject is by no means so inclusive as that previously treated. As stated, this paper is merely a record of tests made in a practical manner on two useful series of alloys, and is not at all a critical study of their properties.

14-KARAT ALLOYS

These alloys are important because they are the most generally used in 14-kt. jewelry; by changing the proportions of silver and copper there are obtained all shades of color from the green of the alloy containing gold and silver but no copper, to the red of the alloy containing gold and copper but no silver. Many 14-kt. gold alloys are made with the addition of zinc to the three metals mentioned here; the added metal does not appreciably alter the color of the alloy nor has it, in general, much effect on the working properties; it may, however, prove useful as part of the zinc added may act as a deoxidizer and render the alloy free of gas. It is not a necessary addition because with proper precautions all the 14-kt. gold alloys containing only silver and copper in addition to the gold can be made free of gas and capable of being cold rolled without cracking. The alloys in which approximately equal quantities of silver and copper

* Baker & Co., Inc.

¹ E. Jänecke: Das ternäre System Kupfer, Silber, Gold. *Metallurgie* (1911) **8**, 597.

L. Sterner-Rainer: Einige Eigenschaften der Legierungen Au-Ag-Cu. *Zeitschr. für Metallkunde* (May, 1926) **18**, 143, and Rekristallisation und Entfestigung von Edelmetalllegierungen (June, 1927) **19**, 245.

are present (Nos. 7 and 8) have a tendency to crack somewhat on rolling and to break on wire drawing; in these cases the addition of a little zinc is beneficial.

The various alloys used for the experiments are given in Table 1; the gold, of course, was kept at 58.33 per cent., the silver varied from 41.67 per cent. to none and the copper from none to 41.67 per cent.

Melts of 12 oz. were used. The requisite amounts of the pure metals were weighed out, placed in a No. 1 graphite crucible, and completely covered with powdered charcoal. The alloys were poured at a moderate heat into a split iron mold giving an ingot 2 by 2 by $\frac{3}{8}$ inches.

TABLE 1.—*Composition of Alloys Investigated*

Alloy No.	Au, Per Cent.	Ag, Per Cent.	Cu, Per Cent.
1	58.33	41.67	0
2	58.33	34.97	6.70
3	58.33	33.33	8.34
4	58.33	31.25	10.42
5	58.33	29.67	12.00
6	58.33	27.77	13.90
7	58.33	22.92	18.75
8	58.33	20.83	20.84
9	58.33	18.75	22.92
10	58.33	16.00	25.67
11	58.33	12.00	29.67
12	58.33	10.42	31.25
13	58.33	8.34	33.33
14	58.33	6.70	34.97
15	58.33	0	41.67

Color

There is a gradual transition in color from the green of No. 1 to the red of No. 15; alloys No. 1 to 6 may be classed as green golds, No. 7 to 10 as yellow golds, and No. 11 to 15 as red golds.

Specific Gravity

The specific gravities were first determined for the alloys in the cast form and a correction made so as to give the specific gravity at 15.5° C. (60° F.). The ingots were then cold rolled to $\frac{1}{4}$ in. and the specific gravities redetermined.

It will be observed from Table 2 that in many cases the specific gravity of the rolled alloy is materially greater than that of the same alloy in the cast condition. A slight increase is expected, due to a real change of gravity of the alloy by rolling, but the larger increases are due to the fact that the alloy, as cast, contained a certain amount of gas

TABLE 2.—*Specific Gravity of Cast and Hard-rolled 14-kt. Alloys*

Alloy No.	Cast Alloys		Hard-rolled Alloys	
	Specific Gravity	Troy Oz. per Cu. In.	Specific Gravity	Troy Oz. per Cu. In.
1	14.35	7.56	14.42	7.60
2	14.02	7.39	14.02	7.39
3	13.72	7.23	13.99	7.37
4	13.72	7.23	13.91	7.32
5	13.52	7.13	13.86	7.30
6	13.59	7.16	13.78	7.26
7	13.60	7.17	13.58	7.16
8	13.28	7.00	13.50	7.11
9	13.43	7.08	13.47	7.10
10	13.09	6.90	13.30	7.01
11	13.06	6.88	13.14	6.92
12	13.00	6.85	13.13	6.92
13	12.90	6.80	13.02	6.86
14	12.90	6.80	12.95	6.82
15	12.50	6.59	12.71	6.70

which compresses more than the alloy itself on rolling and thus effects an apparent considerable increase in specific gravity. The results in Table 2 are given diagrammatically in Fig. 1.

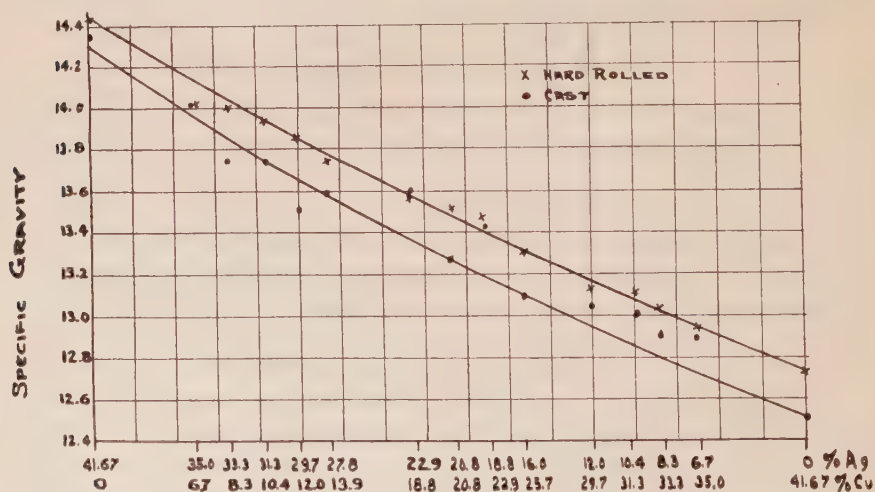


FIG. 1.—COMPOSITION OF 14-KT. GOLD, SILVER, COPPER ALLOY; BASED ON RESULTS IN TABLE 2.

These determinations show that a simple method for finding out whether a metal or alloy is "gassed" is to measure the specific gravity in the cast state and in the cold-rolled state; if there is much difference in specific gravity the ingot has gas inclusions.

Brinell Hardness

The hardness of the alloys was first measured in the ingot as cast by a Baby Brinell machine, 2-mm. ball, 120-kg. load. The alloys were then cold rolled without annealing from $\frac{3}{8}$ in. thickness to $\frac{1}{8}$ in. thickness and the hardness determined in the hard-worked condition. The rolled alloys were then cut up into pieces $\frac{3}{4}$ by $\frac{1}{2}$ by $\frac{1}{8}$ in. and put into an elec-

TABLE 3.—*Brinell Hardness of 14-kt. Alloys, Cooled Slowly*

Alloy No.	Cast	Hard Worked	Cooled Slowly after Annealing at						
			400° C.	500° C.	550° C.	600° C.	650° C.	700° C.	800° C.
1	53	115	120	112	69	64	62	59	56
2	118	210	242	218	148	140	138	128	116
3	144	240	278	240	179	166	162	168	150
4	170	278	300	278	234	224	226	242	230
5	217	270	310	285	251	250	255	258	255
6	242	286	332	293	240	272	278	270	258
7	250	322	330	280	227	217	267	250	237
8	250	320	342	269	237	206	260	251	250
9	290	335	342	285	234	215	267	263	239
10	255	322	342	292	233	231	250	237	258
11	206	302	320	255	226	214	220	210	194
12	183	286	300	264	190	174	165	167	161
13	172	282	282	242	200	170	179	179	160
14	154	276	282	242	192	160	165	160	144
15	113	268	242	174	156	130	130	126	110

TABLE 4.—*Brinell Hardness of 14-kt. Alloys, Quenched*

Alloy No.	Cast	Hard Worked	Quenched after Annealing at						
			400° C.	500° C.	550° C.	600° C.	650° C.	700° C.	800° C.
1	53	115	110	110	65	62	59	56	54
2	118	210	234	195	168	110	108	111	102
3	144	240	258	200	148	131	130	128	117
4	170	278	288	245	240	166	144	143	140
5	217	270	302	251	242	180	160	160	152
6	242	286	302	270	242	200	170	174	160
7	250	322	330	215	212	203	167	184	201
8	250	320	340	243	225	217	183	181	198
9	290	335	340	251	214	220	181	172	186
10	255	322	338	254	220	206	167	190	172
11	206	302	302	235	224	198	182	178	170
12	183	286	312	237	186	176	165	145	143
13	172	282	282	201	188	168	170	166	152
14	154	276	265	186	176	166	163	150	139
15	113	268	220	166	139	126	129	124	108

trically heated furnace for annealing. Tests were made for each piece at 400°, 500°, 550°, 600°, 650°, 700°, 800° C., the alloy being kept in the furnace for 5 min. after the sample had reached the furnace temperature; in each case one piece was allowed to cool slowly in the air after removing from the furnace and a second piece of the same alloy was removed and quickly quenched in water. Tables 3 and 4 give the results obtained.

The figures for hardness in the hard-rolled and in the cast condition are given, together with the ratio of these hardnesses, in Table 5.

TABLE 5.—*Hardness of Hand-rolled and Cast Alloys and Ratio of Hardness*

Alloy No.	Hardness, Hard-rolled	Hardness, Cast	Ratio of Hardnesses
1	115	53	2.17
2	210	118	1.78
3	240	144	1.67
4	278	170	1.65
5	270	217	1.24
6	286	242	1.18
7	322	250	1.28
8	320	250	1.28
9	335	290	1.15
10	322	255	1.26
11	302	206	1.47
12	286	183	1.56
13	282	172	1.64
14	276	154	1.79
15	268	113	2.37

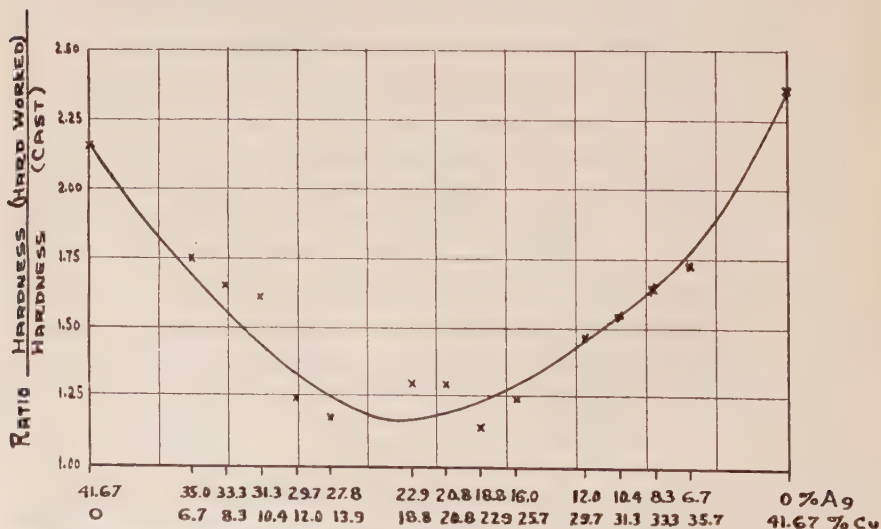


FIG. 2.—COMPOSITION OF 14-KT. GOLD, SILVER, COPPER ALLOY; BASED ON RESULTS IN TABLE 5.

The results in Table 5 are plotted in Fig. 2, the abscissa being the percentages of silver and copper and the ordinate the ratio of the hardness. It will be seen that the hardening effect of rolling is considerable where either silver or copper is greatly in excess of the other metal and that the alloys where silver and copper are in about equal proportions do not harden much on rolling.

Another feature of interest is the initial hardening which the alloys undergo when the hard-worked material is heated to a temperature somewhat below that at which softening begins. This phenomenon seems to be a general one in metals and alloys and has not yet received adequate explanation. Examination of Tables 3 and 4 will show that there does not seem to be any connection between the composition of the alloy and the magnitude of this initial hardening. It was thought worth while to examine this phenomenon more closely in the case of one of the alloys of the series, and No. 4 was chosen for the purpose. A new melt of this alloy was made and the ingot rolled down from $\frac{3}{8}$ to $\frac{1}{8}$ in. thick without annealing; the Brinell hardness was 269. Test pieces of the hard-rolled material were immersed in a bath of molten potassium nitrate at a temperature of 400° C. The time of immersion varied from 15 sec. to 2 hr. The hardness values obtained were:

15 sec.....	298	10 min.....	269
30 sec.....	302	15 min.....	269
60 sec.....	300	30 min.....	253
90 sec.....	300	60 min.....	215
2 min.....	293	120 min.....	183
5 min.....	283		

It will be observed therefore that the maximum temporary increase in hardness is reached within a very short time after subjecting the alloy to the annealing temperature; the transitory nature of the phenomenon probably explains both the apparent absence of an increase in hardness in some cases and the nonuniformity of such an increase in others of the alloys in Tables 3 and 4 in which 5-min. periods were used. In this connection it might be mentioned that alloy No. 4 showed no change in hardness after boiling in water for 17 hr. It is interesting to compare these results with those given by Sterner-Rainer.

Examination of Tables 3 and 4 will show that, in general, the slowly cooled alloys are considerably harder than the quenched alloys; this increase in hardness of the alloys in passing through a certain range of temperature is observable in every case where gold and copper are present, irrespective of the presence of other metals in the alloy. Similar results were obtained by Kurnakow and Zemczuzny,² who explained the

² N. Kurnakow and S. Zemczuzny: *Über die Legierungen des Kupfers mit Nickel und Gold. Die elektrische Leitfähigkeit der festen Metallösungen. Zeitschr. anorg. Chem.* (1907) **54**, 159. N. Kurnakow, S. Zemczuzny and M. Zasedatelev: *The Transformations in Alloys of Gold with Copper. Jnl. Inst. Met.* (1916) **15**, 305.

phenomenon by stating that some sort of a compound of gold and copper is formed in the solid state when the alloys are slowly cooled from the fusion point to atmospheric temperature but that when the material is quenched, the range of formation of the compound is passed so quickly that the compound has not the opportunity to form and the quenched alloy is much softer than the slowly cooled alloy.

Tensile Strength

The tensile strength of the alloys was measured on wires of 0.002 in. dia. and in the hard drawn condition. A balance beam was used for the purpose, the wire being stretched to the breaking point by gradually running mercury into a container suspended from the other end of the balance beam. The figures in Table 6 are the weights of mercury, in ounces avoirdupois, which had been run in when the wire snapped.

TABLE 6.—*Tensile Strength of 14-kt. Alloys*

Alloy	Tensile Strength Oz. (Avoir:)
1	3.8
2	7.2
3	7.1
4	8.0
5	9.1
6	8.8
7	10.1
8	9.9
9	10.0
10	8.8
11	10.2
12	9.4
13	10.0
14	10.4
15	8.8

The tensile strengths in the table do not show any regularity with regard to composition; this is probably due to the difficulty of obtaining fine wires in exactly the same condition, for a slight difference in the amount of draft given on rolling down would somewhat affect the results. Attention need only be drawn to the comparatively weak gold-silver alloy No. 1.

Erichsen Test for Ductility

These tests were made on sheets of the various alloys $3\frac{1}{4}$ by $3\frac{1}{4}$ by 0.040 in. in a standard Erichsen machine; one set of readings was obtained on sheets annealed at 750° C. and cooled slowly and another set of readings on sheets annealed at the same temperature and quenched (Table 7).

TABLE 7.—*Erichsen Number of 14-kt. Alloys*

Alloy	Erichsen Number	
	Cooled Slowly	Quenched
1	11.4	11.3
2	10.3	9.7
3	9.2	10.1
4	8.0	9.6
5	8.1	10.5
6	7.8	9.1
7	7.3	7.9
8	6.9	8.9
9	7.6	9.4
10	7.6	9.0
11	8.9	8.9
12	9.5	9.2
13	10.0	9.9
14	10.3	10.3
15	11.3	11.4

It will be observed that alloys 1 and 15 have about the same ductility; that is, 41.67 per cent. of either silver or of copper have the same effect on gold. The addition of copper to the gold-silver alloy or the addition of silver to the gold-copper alloy causes a gradual decrease in the ductility and the alloys with the lowest ductility are those in which the proportions of copper and silver are approximately equal. The table is of interest as it shows the effect of quenching on the ductility of the alloy; 1 and 2 at the silver end and 11, 12, 13, 14 and 15 at the copper end are not rendered more ductile by quenching but the effect is quite distinct in the alloys from 3 to 10. This indicates that there is formed, as discussed in a previous paragraph, a harder and less ductile compound on slowly cooling those alloys in which copper lies between 8.34 and 25.67 per cent.

Melting Points

The melting points were determined by carefully heating in an electric tube furnace a loop of wire, about 0.030 in. dia., which was connected to a platinum wire at one end and a platinum-ten per cent. rhodium wire at the other. The temperature was read by means of a sensitive millivoltmeter and the heating was carried out in a hydrogen atmosphere to prevent oxidation. The temperature at which the millivoltmeter reading dropped to zero indicated the breaking of the circuit by fusion of the gold alloy wire. Table 8 gives the results obtained; the column marked Jänecke gives figures taken from the paper by Ernst Jänecke.

TABLE 8.—*Melting Point of 14-kt. Alloys*

Alloy	Melting Point, Deg. C.	Jänecke, Deg. C.
1	1021	1023
2	930	917
3	909	905
4	887	888
5	879	875
6	861	862
7	837	845
8	838	838
9	842	846
10	847	853
11	860	867
12	870	872
13	873	880
14	881	888
15	922	922

Electrical Resistance

The resistance was measured on 10 ft. of the hard drawn wire of 0.010 in. dia. by means of a Wheatstone bridge. The results given in Table 9 are for a temperature of about 20° C.

TABLE 9.—*Electrical Resistance of 14-kt. Alloys*

Alloy	Electrical Resistance	
	Ohms per Mil Ft.	Microhms per Cm. Cube
1	56.8	9.4
2	64.4	10.7
3	63.6	10.6
4	65.2	10.8
5	66.0	11.0
6	66.8	11.1
7	69.2	11.5
8	69.2	11.5
9	70.0	11.6
10	70.0	11.6
11	74.4	12.4
12	70.8	11.8
13	69.2	11.5
14	69.2	11.5
15	66.8	11.1

The figures indicate that the alloys at the silver end of the series have a lower electrical resistance than those at the copper end.

Electromotive Force

The electromotive force of the various alloys was measured against chemically pure platinum in an electrically-wound tube furnace kept at 800° C. The wires used were 0.0236 in. dia. and were annealed before testing.

TABLE 10.—*Electromotive Force of 14-kt. Alloys*

Alloy	E. M. F. against Pt at 800° C. M.v.
1	8.25
2	8.84
3	8.95
4	9.25
5	9.47
6	9.56
7	9.60
8	9.80
9	9.80
10	9.85
11	9.65
12	9.75
13	9.15
14	9.80
15	10.26

Table 10 shows that the alloys with higher copper content give the greater electromotive force against platinum, that containing gold and copper only having the greatest value of the whole series.

18-KARAT ALLOYS

The 18-kt. alloys are important because they are most generally used in 18-kt. jewelry; by changing the proportions of silver and copper there are obtained all shades of color from the green of the alloy containing gold and silver but no copper, to the red of the alloy containing gold and copper but no silver. If the addition of zinc is useful as a deoxidizer and renders the 14-kt. gold alloys free from gas, it is not such a desirable addition to the 18-kt. gold alloys of copper and silver. These are more easily cast free from gas than the 14-kt. alloys and with the exception of the alloy containing only gold and copper are readily rolled without cracking.

The various alloys used for the experiments are given in Table 11; the gold, of course, was kept at 75 per cent., the silver was varied from 25 to none and the copper from none to 25 per cent.

Melts of 15 oz. were used. The requisite amounts of the pure metals were weighed out, placed in a No. 1 graphite crucible and completely covered with powdered charcoal. The alloys were poured at a moderate heat into a split iron mold giving an ingot 2 by 2 by $\frac{3}{8}$ inches.

TABLE 11.—*Composition of Alloys Investigated*

Alloy No.	Au	Ag	Cu
1	75.0	25.0	0
2	75.0	22.0	3.0
3	75.0	20.0	5.0
4	75.0	19.0	6.0
5	75.0	17.0	8.0
6	75.0	14.0	11.0
7	75.0	13.0	12.0
8	75.0	12.5	12.5
9	75.0	12.0	13.0
10	75.0	11.0	14.0
11	75.0	8.0	17.0
12	75.0	6.0	19.0
13	75.0	5.0	20.0
14	75.0	3.0	22.0
15	75.0	0	25.0

Color

There is a gradual transition in color from the green of No. 1 to the red of No. 15; alloys 1 to 5 may be classed as green golds, 6 to 10 as yellow golds, and 11 to 15 as red golds.

Specific Gravity

The specific gravities were first determined for the alloys in the cast form and a correction made so as to give the specific gravity at 15.5° C.

TABLE 12.—*Specific Gravity of 18-kt. Alloys*

Alloy No.	Cast Alloys		Hard-rolled Alloys	
	Specific Gravity	Troy Oz. per Cu. In.	Specific Gravity	Troy Oz. per Cu. In.
1	16.02	8.44	16.02	8.44
2	15.85	8.35	15.85	8.35
3	15.77	8.31	15.77	8.31
4	15.61	8.23	15.60	8.22
5	15.57	8.21	15.58	8.21
6	15.19	8.00	15.40	8.12
7	15.31	8.07	15.35	8.09
8	15.05	7.93	15.25	8.04
9	15.03	7.92	15.29	8.06
10	14.97	7.89	15.25	8.04
11	14.84	7.82	15.10	7.96
12	14.84	7.82	15.02	7.92
13	14.85	7.82	14.97	7.89
14	14.67	7.73	14.84	7.82
15	14.59	7.69	14.73	7.76

(60° F.). The ingots were then rolled to $\frac{1}{4}$ in. and the specific gravities redetermined. (Table 12.)

The results in Table 12 are given diagrammatically in Fig. 3.

It will be observed from Table 12 that in many cases the specific gravity of the rolled alloy is greater than that of the same alloy in the cast condition. A slight increase might be expected, due to a real change of gravity of the alloy by rolling, but the larger increases are due to the fact that the alloy as cast contained a certain amount of gas which compressed more than the alloy itself on rolling and thus caused an apparent considerable increase in specific gravity.

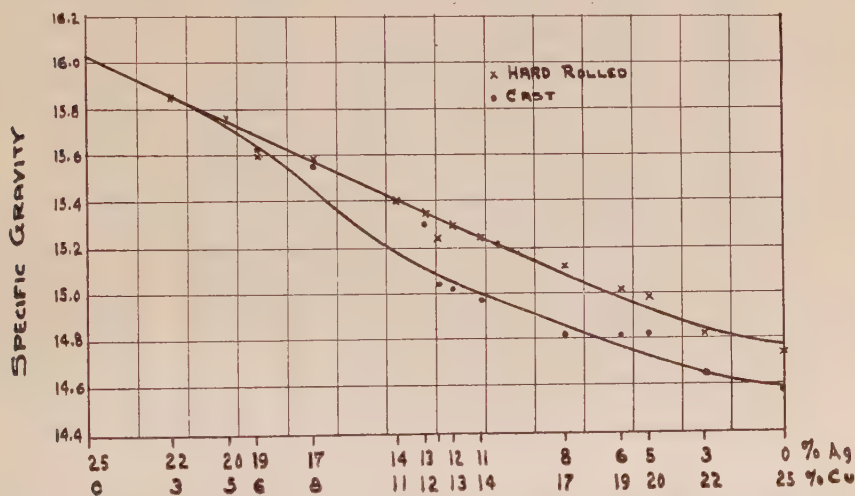


FIG. 3.—COMPOSITION OF 18-KT. GOLD, SILVER, COPPER ALLOYS; BASED ON RESULTS IN TABLE 12.

These determinations show that a simple method of finding out whether a metal or alloy is "gassed" is to measure the specific gravity in the cast state and in the rolled state; if there is much difference in specific gravity the ingot had gas inclusions.

Brinell Hardness

These tests were made in the same way as for those of the 14-kt. golds.

Tables 13 and 14 show that the hardness of the alloys of the series, either in the cast or hard-rolled condition, increases with the copper content. At the same time it will be seen that the degree of hardening on cold rolling is fairly uniform and that, with the exception of the last two alloys, the Brinell number is increased to the extent of 80.

The alloys, with the exception of No. 15 are all easily workable regardless of the method of heat treatment afforded them. With this last alloy

of the series quenching after heating the metal above 500° C. is necessary in order to procure a workable product.

From Tables 13 and 14 it will be seen that the quenched alloys are not appreciably softer than the slowly cooled alloys except in the cases of those high in copper.

TABLE 13.—*Brinell Hardness of 18-kt. Alloys*

Alloy No.	Cast	Hard Worked	Cooled Slowly after Annealing at						
			400° C.	500° C.	550° C.	600° C.	650° C.	700° C.	800° C.
1	45	113	113	70	59	55	54	53	52
2	83	166	166	98	93	83	85	84	82
3	103	188	194	130	108	104	106	102	94
4	117	201	206	151	121	121	121	109	103
5	139	220	220	152	130	130	130	124	112
6	158	234	258	176	172	166	144	138	135
7	170	245	258	179	176	163	144	138	134
8	166	234	258	182	172	168	152	148	144
9	156	265	235	181	162	155	148	145	141
10	166	265	237	201	172	160	156	156	145
11	174	267	251	201	186	167	161	162	156
12	192	282	280	190	196	186	181	170	165
13	224	302	295	190	190	198	196	170	167
14	245	302	302	276	267	237	186	196	162
15	265	321	370	347	342	287	330	323	236

TABLE 14.—*Brinell Hardness of 18-kt. Alloys*

Alloy No.	Cast	Hard Worked	Quenched after Annealing at						
			400° C.	500° C.	550° C.	600° C.	650° C.	700° C.	800° C.
1	45	113	110	85	59	55	54	54	52
2	83	166	161	96	92	85	83	84	82
3	103	188	188	155	110	106	104	101	98
4	117	201	201	170	121	120	114	109	104
5	139	220	214	194	130	129	128	122	112
6	158	234	255	174	152	144	139	134	130
7	170	245	245	174	152	146	142	138	130
8	166	234	258	198	156	154	152	144	138
9	156	265	237	204	156	148	148	139	137
10	166	265	237	194	161	150	150	145	140
11	174	267	253	204	162	154	156	147	141
12	192	282	263	196	172	165	160	152	148
13	224	302	267	198	181	172	167	160	156
14	245	302	323	186	172	162	167	156	160
15	265	321	343	186	178	167	176	156	167

The figures for hardness in the hard-rolled and in the cast condition are reproduced, together with the ratio of these hardnesses, in Table 15.

TABLE 15.—*Hardness of Hard-rolled and Cast Alloys and Ratio of Hardness*

Alloy No.	Hardness, Hard-rolled	Hardness, Cast	Ratio of Hardnesses
1	113	45	2.51
2	166	83	2.00
3	188	103	1.82
4	201	117	1.72
5	220	139	1.58
6	234	158	1.48
7	245	170	1.44
8	234	166	1.41
9	265	156	1.70
10	265	166	1.60
11	267	174	1.53
12	282	192	1.47
13	302	224	1.35
14	302	245	1.23
15	321	265	1.21

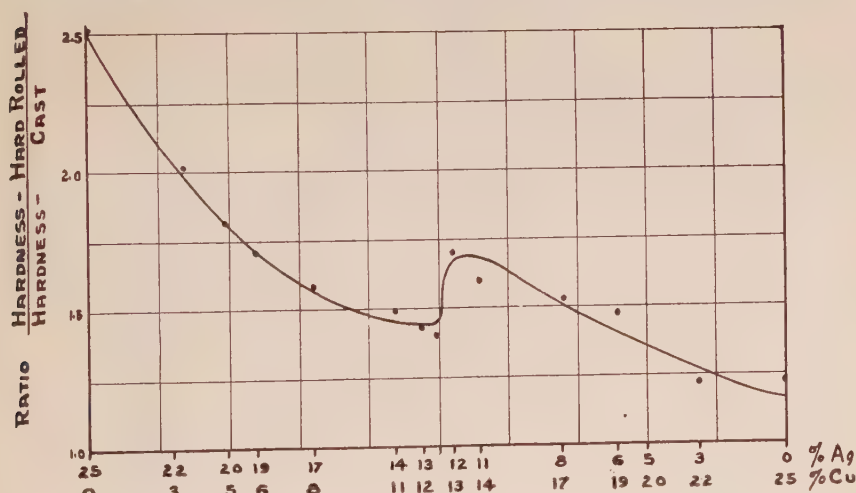


FIG. 4.—COMPOSITION OF 18-KT. GOLD, SILVER, COPPER ALLOYS; BASED ON RESULTS IN TABLE 15.

The results in Table 15 are plotted in Fig. 4, the abscissa being the percentage of silver and copper and the ordinate the ratio of the hardness. It will be seen that the hardening effect of rolling is considerable in the case of the high-silver alloys whereas the effect is comparatively small with those containing much copper.

Tensile Strength

The tensile strength of the alloys was measured as in the case of the 14-kt. golds. (Table 16.)

TABLE 16.—*Tensile Strength of 18-kt. Alloys*

Alloy	Tensile Strength, Oz. (Avoir.)
1	3.6
2	6.1
3	6.4
4	6.8
5	8.0
6	8.4
7	8.5
8	8.6
9	8.7
10	8.8
11	8.2
12	8.9
13	9.1
14	9.4
15	9.3

Alloy No. 1 is therefore much weaker than the remaining members of the series; increasing the copper content increases the tensile strength.

Erichsen Test for Ductility

These tests were made on sheets of the various alloys as in the 14-kt. golds. (Table 17.)

TABLE 17.—*Erichsen Number of 18-kt. Alloys*

Alloy	Erichsen Number	
	Cooled Slowly	Quenched
1	7.3	13.0
2	6.5	11.7
3	5.3	11.4
4	4.8	11.6
5	3.8	11.0
6	3.1	10.0
7	3.5	9.8
8	3.6	9.5
9	3.8	10.0
10	2.5	8.2
11	2.9	8.8
12	3.2	8.4
13	2.9	7.9
14	2.6	5.8
15		

The ductility therefore decreases uniformly with the increase in the copper, both in the slowly cooled and in the quenched condition. It was not possible to obtain a satisfactory sheet for test in the case of No. 15.

Melting Points

The melting points were determined as before. Table 18 gives the results obtained; the column marked Jänecke gives figures taken from the paper by E. Jänecke.

TABLE 18.—*Melting Point of 18-kt. Alloys*

Alloy	Melting Point, Deg. C.	Jänecke, Deg. C.
1	1037	1032
2	1000	975
3	964	941
4	952	935
5	935	918
6	900	898
7	892	895
8	902	893
9	881	890
10	873	880
11	869	878
12	885	878
13	880	879
14	887	881
15	897	

Electrical Resistance

The resistance was measured in the same way as in the 14-kt. alloys. The results given in Table 19 are for a temperature of about 20° C.

TABLE 19.—*Electrical Resistance of 18-kt. Alloys*

Alloy	Electrical Resistance	
	Ohms per Mil Ft.	Microhms per Cm. Cube
1	59.5	9.9
2	64.6	10.7
3	67.6	11.2
4	69.3	11.5
5	71.3	11.9
6	74.0	12.3
7	75.5	12.6
8	75.1	12.5
9	76.1	12.7
10	77.1	12.9
11	78.7	13.1
12	79.4	13.2
13	79.9	13.3
14	81.0	13.5
15	82.1	13.7

The alloys at the silver end of the series have a lower electrical resistance than those at the copper end.

Electromotive Force

The electromotive force of the various alloys was measured as in the 14-kt. golds.

TABLE 20.—*Electromotive Force of 18-kt. Alloys*

Alloy	E. M. F. against Pt at 800° C. M.v.
1	7.90
2	8.20
3	8.20
4	8.35
5	8.40
6	8.62
7	8.80
8	8.50
9	8.70
10	9.10
11	8.95
12	8.95
13	8.70
14	8.50
15	8.60

The alloy containing only gold and silver has, therefore, the lowest value but there does not appear to be any regularity in the other members of the series.

DISCUSSION

E. M. WISE, Bayonne, N. J.—In reply to Dr. Carter's request for an etching reagent suitable for gold and silver alloys, I would suggest the use of a mixture of equal parts of 10 per cent. solutions of ammonium persulfate and potassium cyanide. This etching reagent is effective only for a short time after mixing, but is the most generally useful solution available. It is particularly desirable for silver content alloys, where so many other etching solutions fail on account of the formation of insoluble films on the specimen. The same solution is also very effective for palladium alloys.

The age-hardening observed in some of the gold, silver, copper alloys is of both theoretical and practical interest, and while it may be observed in hard-rolled alloys it is most clearly shown by observing the changes in hardness of material which has been previously annealed and quenched.

In Fig. 5 the variation in hardness of a 10-kt. yellow gold alloy, after aging at various temperatures for one hour, is shown. The curves are shown, one for material which has been reduced 50 per cent. by cold rolling, and the other for material which has been annealed at 750° C. and quenched in oil. The hardness values on the K scale were determined with the Rockwell hardness tester using 100-kg. load and the diamond cone. The equivalent B and C scale readings are also given.

G. F. KUNZ, New York, N. Y.—Would you call it 10-kt. gold? There is not more than one-third gold in bulk. But anyway, by weight, there are 14 parts alloy and 10 gold. The specific gravity of the alloy would be nearly 50 per cent. lighter, so virtually there is not one-half gold.

E. M. WISE.—The 10-kt. was chosen arbitrarily. The same phenomena are observed in 14-kt. and higher karat gold alloys.

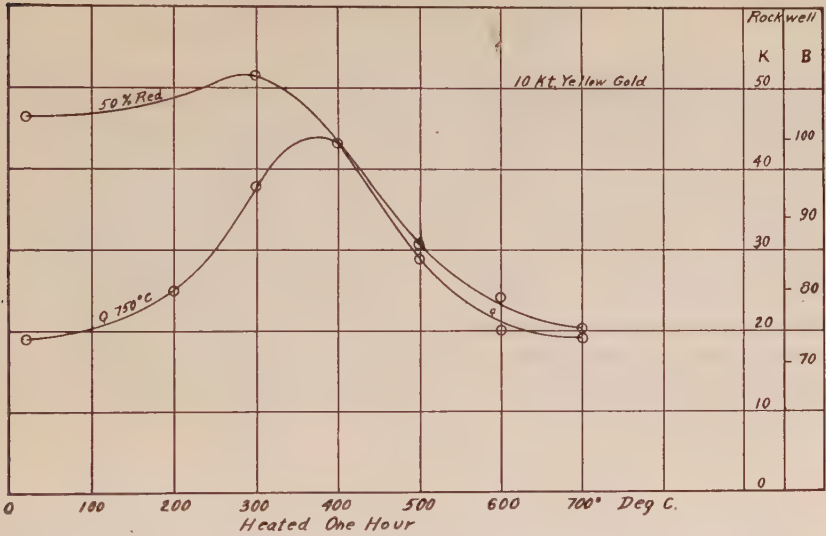


FIG. 5.—ANNEALING AND AGING CHARACTERISTICS OF A 10-KT. YELLOW GOLD ALLOY.

E. A. CAPILLON.—These alloys are subject to the same disease as brass. We find that season cracking occurs in 10-kt. gold as in brass. We have also found that we can do away with that by annealing at a low temperature around 700° or 800° F. Annealing at that temperature prevents season cracking, and there is a noticeable increase in hardness. I believe this is in accordance with the results given in this paper.

Use of the Noble Metals for Electrical Contacts

By E. F. KINGSBURY,* NEW YORK, N. Y.

(New York Meeting, February, 1928)

ONE of the well-known and important uses of the noble or precious metals has been for electrical contacts. In fact, the elements of this group, comprising gold, silver and the six platinum metals, have been called "noble" because of their ability to resist heat and corrosion, properties which were early found to be of importance in good contacts. Of these, platinum and its iridium alloys, palladium, and silver, have been extensively used. In recent years the electrical industry has been responsible for about one-eighth of the total consumption of the platinum metals in the United States. Information is not available as to what part of this one-eighth has been used for contacts but it is certainly an important one.

SUBSTITUTES FOR PLATINUM

During the past 20 years a considerable number of contact alloys have been proposed in the patent literature largely with the aim of more or less replacing platinum by gold or silver, and some of these alloys are finding increasingly widespread application as the reliability of their performance becomes established. From even the partial data at hand it appears that this substitution by the less precious metals has replaced at least one-half of the amount of platinum that the entire electrical industry would otherwise be consuming at the present time.

While the subject is of considerable interest to the metallurgist it is even more so to the electrical engineer and it is surprising that the literature records no systematic and comprehensive investigation along these lines. Practically all the scattered work on noble metal contacts has centered around platinum as a standard and has had two more or less distinct aims. One of these has been the replacement of platinum by cheaper materials, and the other, the development of materials of superior electrical performance. The merit of a contact metal has been assumed to be dependent on its infusibility, and since the more precious metals have the higher melting points there has naturally been an association of the two qualities in the sense that the more precious were

* Bell Telephone Laboratories, Inc.

supposed to be of superior performance. This belief, combined with a lack of understanding of the electrical requirements, has undoubtedly retarded the widespread application of the less precious alloys.

In spite of this condition, however, the use of cheaper platinum substitutes for contacts, as for other technical applications, has been forced by the economic situation. The unstable and continually mounting price of platinum, uncertainty regarding its supply, and the increasing demand have furnished strong incentives to experiment with substitutes. All of this has resulted in important savings to the industry. Although at the present time the price of platinum is declining and the production is increasing, it is very unlikely that the use of substitutes will be diminished, especially as these substitutes are in many cases actually proving superior to platinum.

There are on the market several alloys of the platinum metals that are used because they are superior to platinum in melting point and hardness and there are certain types of circuits and conditions where they are demanded, regardless of cost, because of their increased resistance to erosion. Probably the most extensively used of this class are the alloys of platinum with iridium. There are several of these in use up to about 25 per cent. iridium. As the cost increases with the iridium content, the percentage is ordinarily limited approximately to the demands of the circuit. An alloy of platinum, iridium and rhodium has been found to be of superior performance to the iridium series and is used where the binary alloys are not satisfactory.

LACK OF RESEARCH ON ELECTRICAL CONTACTS

There is probably no element in an ordinary electrical circuit so little understood as the contacts. Certainly little is known concerning the physical and chemical phenomena associated with the interruption and closure of circuits. Complex reactions are produced not only in the atmosphere itself but between it and the elements composing the electrodes, which tend to produce more or less insulating films and which may result in the ultimate destruction of the contacts for practical purposes. It is of course well known that the conduction of electricity by gases depends upon their being ionized and that in this condition they are exceedingly active chemically. This fact combined with a wide range of temperature attained by particles and localized areas on the surface of the electrodes, makes possible the formation of compounds that are very critical regarding the conditions necessary for their production and existence. A good example is the formation of the oxides of the noble metals, many of which are difficult to produce and which exist only within a comparatively narrow range of temperature at atmospheric pressure.

DEPENDENCE OF BEHAVIOR ON FORM OF DISCHARGE

A large amount of study has been devoted to discharges between stationary electrodes so that their general characteristics are fairly well understood. The mere fact that as contacts the electrodes are in motion does not fundamentally alter their nature. The difficulty arises when an attempt is made to explain, in detail, the electrical discharges occurring with moving electrodes as they occur in a variety of forms and even in a single transient discharge there may be a succession of different forms. Furthermore the effect on the electrodes may be very radically altered as the type of the discharge changes. Some forms produce very little disintegration of the electrodes, while others produce a great deal. With some the melting point appears to be of great importance while with others it does not seem to be of any importance within wide limits. With some metals, a slight modification of the discharge may shift the predominating loss from one electrode to the other. This situation is of importance metallurgically because it means that the composition and size of the contacts must be carefully adapted to the type of circuit if the most satisfactory service is to be secured at a minimum cost of installation and maintenance.

IMPORTANCE OF MECHANICAL CONDITIONS

In any discussion of contacts there is one elementary factor which should be kept in mind and yet which is so frequently overlooked, judging from the inquiries and suggestions received, that it should be mentioned here. This factor is the mechanical conditions under which the contacts operate. It is obvious that in many cases it determines the choice of material. A delicate relay with a contact pressure of only a few grams demands a noble metal, whereas a heavy pressure sliding contact in a switch can be made of copper. In an automobile ignition interrupter it may be possible to use tungsten whereas in a telephone relay, tungsten may be a total failure. These examples are sufficient to emphasize the important influence of the mechanical conditions on the metallurgical aspect of the subject. It is fortunate for the electrical engineer that in many cases there has been considerable latitude in the mechanical design for, of recent years, it has permitted an enormous number of base metal contacts to be used in circuits of low power such as automotive ignition, radio sets and dial telephone systems. There are, however, many circuits where the power available for the operation of contacts is so small and the pressure so limited that only carefully selected noble metals will function properly. This applies especially to a large number of telephone and telegraph circuits and the discussion given in this paper is based largely on a study of them. However, the results are of general interest and application.

Some stress has previously been laid on the economic aspect because of its influence on the development of the subject and because of its increasing importance with the expansion of the telephone industry. In addition, reference has been made to contact performance. For our purpose this term covers three factors: Contact resistance, the erosion of the electrodes and the building up of objectionable projections due to the transfer of metal from an eroded electrode to the opposite one.

CONTACT RESISTANCE

The importance of the first factor is so obvious that it hardly needs to be mentioned, for unless a metal consistently gives a low and steady resistance at the contact junction it is unsatisfactory. In service the number of operations very frequently runs into many millions over a long period of time and there must be the minimum tendency for objectionable oxides and dirt to accumulate. In addition the thickness of the contacts must be proportioned so that the erosion will not wear it away sufficiently to penetrate to the base-metal support, and when the contact is put in service the pressure and maximum separation of the electrodes must be carefully adjusted according to certain standards. In spite of all this control failures occur even with the best materials available. An unknown percentage of failure is no doubt due to dust from the atmosphere even though every precaution may be taken to avoid it by covering the contacts and filtering the air. This type of failure obviously cannot be prevented by any selection of material. Under the best conditions, many noble metals have so few failures per million operations that it is difficult to distinguish between them and to decide which is the better one to use. However, a small difference in this respect may be important not merely because of the reduction in the number of interruptions to the service but because the cost of the maintenance required to correct an increased number of failures may more than offset any initial saving in contact metal.

It should be understood that the value of resistance at which a contact failure occurs, that is, at which the circuit fails to function, is not fixed but depends on the particular circuit. The resistance of a good noble metal contact is only a small fraction of an ohm and is usually so much smaller than that of the circuit which it is operating that there is a large margin of safety. However, if the resistance of a contact much exceeds its normal value, it tends to become unstable and microphonic; that is vibrations of the apparatus produce fluctuations in the resistance. This condition is very objectionable especially if it occurs in a speech transmission circuit.

An excellent illustration of the significance of contact resistance is given by silver. The question occasionally comes up as to why pure

silver cannot be used more extensively. Its low cost is attractive and one could well afford to use large contacts to offset any increased erosion. The answer is that silver and very high silver alloys are of very uncertain resistance in light pressure contacts. For example, a comparison of silver and platinum has shown the former to give many more failures in a million operations and practical experience has also confirmed this difference. As is well known, silver tarnishes readily on standing especially in atmospheres such as exist in most cities. In order to avoid an objectionable tarnish it is necessary to alloy silver with more than half its weight of gold. There have been put on the market so-called stainless silvers, which claim to accomplish this result by the use of certain base metals with silver. One examined by the writer still tarnished slightly but the film seemed to be very fragile and loose as it was easily rubbed off. Although there is a possibility that stainless silvers will in time find limited application in certain types of contacts there is little likelihood of their displacing more noble materials.

In addition to tarnishing by sulfur on standing, silver probably oxidizes in electrical discharges. One evidence of this is the fact that silver gives trouble even when the surface is being continually erupted by the discharge and there is very little time for any ordinary tarnishing. There seems to be an impression, which has worked into the literature, that silver is a good contact metal because its oxides are conducting. The writer has not been able to confirm this statement. Tests on the common monoxide carefully prepared have shown it to be of very high resistance even when strongly compressed in thin discs. It is safe to assume in the absence of more complete information that the oxides are of sufficiently high resistance to cause trouble if they accumulate in the junction. However, they are easily decomposed on heating, a fact which tends to keep down their accumulation.

EROSION OF ELECTRODES

The second factor in evaluating contact performance is the erosion of the electrodes. The ideal material of course is one which is entirely unaffected by the various types of electrical discharges. It is needless to say that no such metal is known, although fortunately the erosion can be controlled to some extent by the proper selection of alloys. It is also possible to reduce it in some cases by putting the contacts in chemically neutral atmospheres, but this is obviously very expensive and impractical on any extended scale. On some circuits even the best alloys available erode so severely that it becomes necessary to protect the contacts by suppressing the discharge by auxiliary electrical circuits. Contact protection on a widespread scale however is out of the question due to its expense—it is much cheaper in most cases to tolerate a certain amount

of erosion in spite of the fact that contact engineering is necessary to proportion the thickness, size, and composition of the contacts to the demands of the service.

It is convenient to classify erosion into three types indicative of fundamental differences in the behavior of contact materials and in the qualities demanded for its suppression. These types are distinguished either by the polarity of the electrode suffering the predominating loss or by the form of the discharge. Two of them are in glow (as distinguished from arc) discharges; one in which the cathode suffers the predominating loss and one in which this loss shifts to the anode. The third type occurs in capacity discharges.

FIRST TYPE OF EROSION—GLOW DISCHARGE

The first and most important type of erosion is that occurring in a large number of glow discharges produced ordinarily when a low energy circuit is interrupted in air. An examination of the electrodes in a case of this type will show some erosion and loss in weight of the cathode while the anode will probably have acquired a small amount and gained in weight. Frequently the anode also loses some in weight but usually not as much as the cathode. The cathode loss in a glow discharge is ordinarily associated with the fact that the cathode is bombarded by the heavy, positively-charged gas ions and that most of the energy in the discharge is dissipated at the surface of the cathode. The process in the case of contacts in air bears a close analogy to the so-called sputtering of metallic cathodes in low-pressure discharge tubes.

A considerable amount of study has been devoted to this low-pressure sputtering, although at the present time experimenters are not in agreement concerning the precise means by which the particles of metal are detached from the cathode. Several theories have been advanced to account for the phenomenon at low pressures. An early one ascribed the detachment to vaporization, although it was soon shown that the sputtering was independent of the gross heating of the cathode and that considerable loss could occur with very little heating. However, it has never been proved conclusively that it is not a special kind of surface heating and evaporation. Another explanation has been based on the mechanical detachment of the particles either directly as a sort of sand-blasting effect or as a result of disruption by the occluded gases. The third explanation advanced is based on electrochemical grounds and presupposes a chemical combination between the gas and the electrodes, the resultant compound being torn off because it is less adhesive than the metal itself. It seems very unlikely that this explanation can hold in many cases because the inert noble gases produce sputtering. In fact, in many cases the loss follows a rule of increasing with the atomic weight of

the gas so that a heavy one, for example argon, is very efficient. Taken as a whole the evidence indicates that low-pressure sputtering cannot be ascribed entirely to any one cause but that the mechanism varies according to the chemical activity of the gas, the metal and the energy with which the ions strike the cathode.

It is reasonable to suppose that these same general explanations will ultimately be found to hold for the erosion of contacts by glow discharges in the atmosphere. However, the conditions prevailing in the disintegration of contacts are more complex than in low-pressure sputtering experiments so that a somewhat different emphasis may be found necessary.

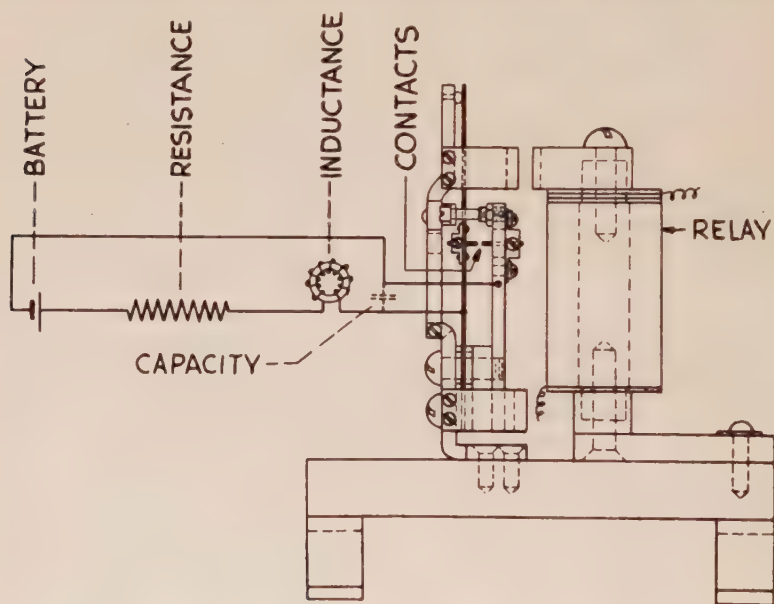


FIG. 1.—CIRCUITS AND RELAY USED IN CONTACT STUDY.

There are of course numerous circuits producing glow discharges on interruption and the energy dissipated in them varies greatly. Some of these discharges produce very little disintegration even over long periods of operation whereas others produce considerable.

The results on the following circuit will be taken as typical of the contact erosion produced by a glow discharge at atmospheric pressure. A steady current of 0.40 amp. flowing through 3 henrys inductance on a battery of 30 volts was interrupted for 1,000,000 times. This circuit¹ and the relay are shown diagrammatically in Fig. 1. The contacts were formed by the abutting, slightly rounded ends of sections of wire 1 mm. dia. held in a relay in such a manner that they could be removed for weigh-

¹ The capacity shown in Fig. 1 was not used until a test described later.

ing before and after testing. The discharge produced by the interruption of this circuit is a typical glow discharge, the voltage at all times being above the minimum of 300 volts necessary to spark in air. In a transient discharge of this nature it is difficult to give an average value of voltage which is effective in determining the energy of the bombarding positive ions because the voltage fluctuates during the course of the transient. The average value, however, in the case under discussion is in all probability from 350 to 400 volts.

Fig. 2 shows the characteristic appearance of contacts of a gold-silver alloy that have been run for 1,000,000 operations on this 30-volt, 0.40-amp., 3-henry circuit. There are plainly visible a mound built up on the anode and a broad, irregular crater worn in the cathode and covering



FIG. 2.—PAIR OF CONTACTS SHOWING EROSION OF CATHODE AND A BUILDING-UP OF ANODE (1,000,000 OPERATIONS).

almost the entire surface. The projection tends to follow the shape of the crater. There is considerable dark brown discoloration over the surface of the anode which the picture does not show clearly. The face of the cathode is kept fairly clean by the discharge but its surface has a dull, mat appearance.

EROSION OF PURE METALS

A series of tests on eight metals resulted in the cathode losses shown in Table 1. In column *A* this loss is given directly in milligrams weight while in *B* it is in volumes and in *C* atomic proportions relative to platinum as unity.

While it is difficult to generalize from the data, they indicate that metals which are similar in chemical valency have approximately equal volume losses. Thus platinum and palladium, iron and nickel, tungsten and molybdenum tend to run the same. It is well known in low-pressure

cathode sputtering that the losses are in many cases proportional to the atomic weight divided by the valence. The comparison in Table 1 of metals of different chemical behavior is uncertain because the average valency that is effective in any instance is not known. It is likely that a mixture of compounds of different valencies are formed and in addition there may be some free metal produced directly. It should be noted however that silver which is ordinarily monovalent has a very high loss while tungsten and molybdenum which may be as high as six have very low losses. Gold is both monovalent and trivalent and its loss is very similar to those for the elements platinum, palladium, iron and nickel.

TABLE 1.—*Cathode Losses in a Glow Discharge, 1,000,000 Operations*

	A	B	C
Platinum.....	1.57	1.00	1.00
Palladium.....	0.94	1.05	1.10
Gold.....	1.39	0.98	0.88
Silver.....	2.67	3.46	3.08
Molybdenum.....	0.32	0.44	0.41
Tungsten.....	0.86	0.62	0.58
Iron.....	0.47	0.81	1.05
Nickel.....	0.53	0.81	1.13

A. Weight loss in milligrams.

B. Volume loss relative to platinum.

C. Loss of atoms relative to platinum.

EROSION IN GASES OTHER THAN AIR

In order to study the influence of the atmospheric corrosion on the disintegration, tests were run on this circuit in a number of gases: hydrogen, nitrogen, oxygen and argon, of which the most interesting are the tests in oxygen and argon. With platinum the loss increased from 1.57 in air to 3.06 in pure oxygen, and fell to 0.25 in purified argon. In general, oxygen caused an increase and argon considerable decrease in the erosion of the elements indicating that oxidation is an important factor in detaching the metal from the cathode. This process therefore appears to be different from the one discussed previously for low pressures where the loss increased with the atomic weight of the gas. Discharge potentials in oxygen are higher and in argon lower than in air and there is a possibility that this may have had an influence also. However, if a cathode is examined under a microscope, films can be seen to form over certain areas which in time are torn off by the discharge. The process appears to be one of alternate oxidation and destruction and is somewhat different from oxidation under ordinary conditions where the protective properties of the film itself are of importance in slowing down the reaction. In the discharge, any film is removed almost as fast as it forms and the metal is constantly exposed to the full action of the gas. In a few cases such as aluminum where the oxide dissociates only at a very high

temperature it appears that the discharge may be unable to remove the protective coating but there is no reason to believe that this is true for most of the metals.

In regard to the action of nitrogen and of hydrogen, in almost every case they produced a decrease in the cathode disintegration. One very notable exception was gold in hydrogen where the loss was in most instances much higher than in air. The abnormal action of hydrogen on gold is of considerable interest because there appears to be some reaction between the two elements. The existence of a gold hydride has not been definitely established in chemical literature but the appearance and abnormal behavior of the electrodes suggests the more or less transient formation of such a compound. Iron was very low on the other hand. Tungsten appeared to be affected by nitrogen as its loss was about the same as in air.

It is interesting to note that platinum and palladium did not lose in hydrogen to anything like the extent that gold did. As is well known, palladium can absorb a considerable amount of hydrogen and this resulted in both electrodes actually gaining somewhat in weight. Platinum acted normally with a cathode loss somewhat more than half that in air and considerably more than in either nitrogen or argon. The behavior of palladium-silver alloys in hydrogen depended on the percentage of palladium, the alloy containing 75 per cent. (by weight) of palladium acting much like the pure metal while 40 per cent. gave a small but decisive cathode loss reflecting the fact that the absorption of hydrogen has been greatly reduced by the presence of 60 per cent. silver. High gold alloys had the enhanced disintegration of gold, the magnitude of the effect being simply diluted.

EROSION OF ALLOYS

The behavior of some of the common elements in the glow discharge has been discussed above. A more interesting and conclusive aspect of the subject is the performance of alloys. For this purpose more than 200 alloys have been studied nearly all of which were made especially for the work in order to control their purity and treatment. In doubtful cases the materials composing the alloys were carefully analyzed and purified and check analyses were made after manufacture. This statement is also true concerning the pure metals tested above. In the case of platinum an unusually high purity was available for check tests.

As typical examples of the behavior of binary solid solutions we will take the two series; silver-palladium and silver-gold. Both of them, according to the best X-ray and thermal evidence available, form complete and unbroken solid solutions from one end to the other and the results are therefore not complicated by variations in their constitution. This restriction is necessary because series which are not completely

soluble give erratic losses and conclusions are difficult. Even in regions where such mixtures are supposedly in solution it is difficult to be certain of the interpretation because the previous treatment may profoundly affect the structure.

Fig. 3 gives the results for silver-palladium and Fig. 4 for silver-gold, both in air on the 30-volt, 0.4-amp., 3-henry circuit previously used. They show the one outstanding characteristic of binary curves, namely, that the losses are greatly reduced in the central portion of the series.

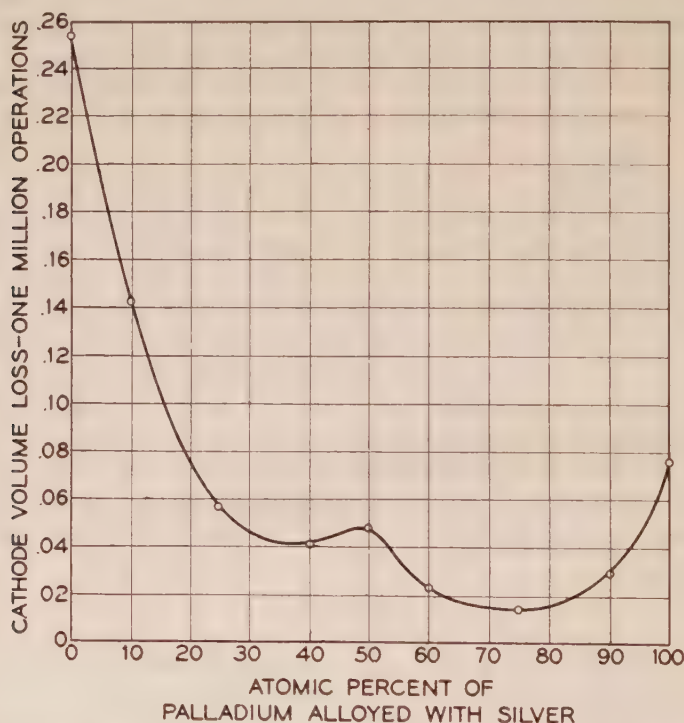


FIG. 3.—VOLUME LOSS OF CATHODE OF SILVER-PALLADIUM ALLOYS IN AN INDUCTIVE DISCHARGE.

It is evident that the addition of either palladium or gold, to silver rapidly decreases the loss until a minimum is reached around 40 per cent. There is then a slight rise followed by a second minimum and finally a rise to the value of pure palladium or gold both of which are much lower than silver. The small maximum in the center is real for it has been checked several times in both instances.

The two examples of Figs. 3 and 4 are given here because they have been studied most carefully and are of most general interest. The U-shape type of curve, however, has been verified for tungsten-molybdenum, platinum-palladium, palladium-nickel and palladium-gold with

the possible exception of a short region near the high gold end. These series are all complete binary solid solutions according to the most reliable evidence. If a series does not form solid solutions throughout the results are more complicated and some of the alloys may show considerably less resistance than either constituent alone. In general such alloys make poor contact materials where they have to withstand discharges similar to the conditions of this test. Under other conditions, of course, complex alloys may be very excellent for contacts.

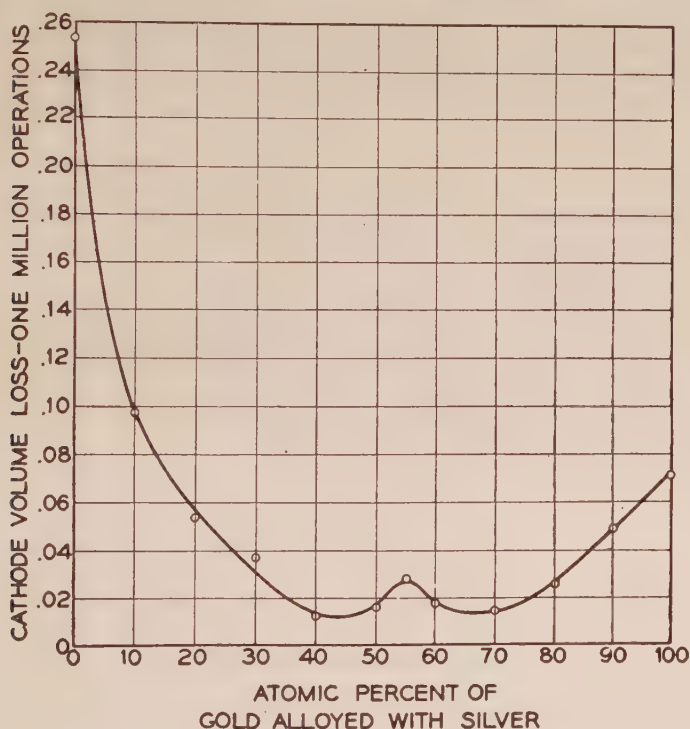


FIG. 4.—VOLUME LOSS OF CATHODE OF GOLD-SILVER ALLOYS IN AN INDUCTIVE DISCHARGE.

The above behavior of the binary solid solutions has not been definitely correlated with any known property of the alloys; the evidence indicates that it is primarily due to an increased resistance to chemical corrosion. Ordinarily in alloys a resistant, non-corrosive element is added which confers that property on the mixture. This is fundamentally different from the behavior shown here in which a degree of resistance is secured which is considerably greater than either constituent alone. It is interesting to note that many contact materials have a decreased erosion together with an increased hardness. The evidence, however, fails to prove any general association of the two qualities

because in many cases the binary alloys can be hardened by third constituents without resulting in an increased resistance to erosion. Furthermore, the silver-gold alloys are very soft and yet are as good as many much harder alloys.

RELATION OF CURRENT TO EROSION

In the circuit used in the above tests, the discharge was secured by interrupting a current of 0.40 amp. If the current is gradually increased another interesting and important effect takes place which will be considered briefly. For each contact material there is a limiting direct current beyond which the disintegration increases so rapidly that it

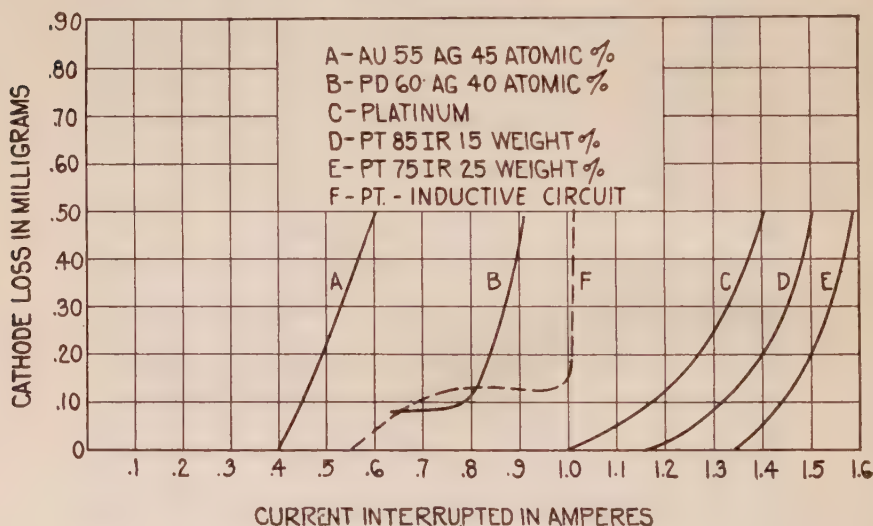


FIG. 5.—CATHODE LOSS OF VARIOUS METALS AS A FUNCTION OF THE CURRENT INTERRUPTED IN A CIRCUIT OF VERY SMALL INDUCTANCE AND 50 VOLTS BATTERY (1,000,000 OPERATIONS).

ordinarily becomes impractical to use it, at least without protection. The effect is best shown by removing the artificial inductance from a circuit such as we have been discussing and obtaining the loss as the interrupted current is gradually increased. Such a circuit will produce only a minute erosion until the limit is reached, at which value the loss suddenly starts to increase rapidly. In Fig. 5 the series of solid curves show the results of such a minimum inductance test on several alloys using a battery of 50 volts. At about 0.4 amp. the disintegration of the gold-silver rapidly increases, at about 0.8 amp. the palladium-silver suddenly changes, at 1 amp. platinum starts to fail and then platinum-15 per cent. iridium and finally the 25 per cent. iridium. Clean tungsten is above any of

these metals but its limiting current gradually decreases with operation due to the accumulation of oxides. Other alloys and metals could be added to this list but these are sufficient to show the characteristic behavior.

The previous results on the limiting current have been with a very small inductance in the circuit and the question naturally arises concerning the effect of increasing it. The presence of inductance does not alter the value of the limiting current though it does affect the absolute magnitude of cathode losses especially at low currents. In Fig. 5 there has been inserted the dashed curve, *F*, to illustrate this point. This curve was obtained on platinum with an inductance added to the circuit in the form of a small relay commonly used in telephone exchanges. Not only are there considerable cathode losses below the limiting current but at that value the losses start to increase much more rapidly than without this inductance. A comparison of curves *C* and *F* clearly shows this difference for platinum and also the very striking fact that the limiting current has not been altered.

The question arises why curves *A*, *C*, *D* and *E* do not approach the axis asymptotically. The reason is that on the "non-inductive" circuit the cathodes in these four cases gained in weight very slightly below the limiting current due to the acquisition of some material from the anodes. These four curves therefore strictly cross the axis and then tend to approach the axis asymptotically. This tendency to cross the axis is also shown by curve *F* just above $\frac{1}{2}$ amp. These reversals have not been shown in Fig. 5 because they are small and the writer does not wish to complicate the illustrations of the limiting currents.

The general explanation of the existence of a limiting current is that as the contacts separate, sufficient heat is generated simultaneously with the attainment of a voltage necessary to initiate an arc discharge, as distinguished from a glow. The arc discharge greatly increases the erosion of the cathodes. An oscillographic examination shows that in general with any appreciable inductance present there is a very transient arc followed by a glow discharge. It is of interest to note that we cannot ordinarily increase the limiting current to any important degree by alloying unless we very considerably raise the melting point at the same time. In some cases the presence of oxides seems to assist in the arcing and destruction of the cathodes so that the limit is increased by placing the contacts in a neutral gas. For all practical purposes however, the limits are fixed. The limiting currents of the five metals in Fig. 5 fall in the order of the melting points, the range being about 845° from the lowest to the highest. This, together with other evidence indicates that the melting point is an important factor in determining the position. There are cases in which apparently the condition and characteristics of the surface at the junction enter and these cases do not fall strictly in

order. The rule, however, is followed sufficiently closely to be of practical importance.

SECOND TYPE OF EROSION—GLOW DISCHARGE

A comprehensive discussion has been given of a typical erosion in a glow discharge. There is frequently encountered a second type of erosion which is characterized by the fact that the transfer of material is in the opposite direction to that discussed previously; that is, the anode is eroded primarily instead of the cathode. Gold and high gold alloys show the most pronounced effect but it occurs with other materials to some extent. Platinum only shows it to a very small degree, silver consider-



FIG. 6.—PAIR OF CONTACTS SHOWING EROSION OF ANODE AND A BUILDING-UP OF CATHODE (1,000,000 OPERATIONS).

ably more so. It is possible, for example, to have the remarkable condition on a circuit in which one contact material will erode and transfer in a given direction and another contact material will go in the opposite direction; the only change having been the composition of the contacts.

The particular types of circuits in which this occurs are usually those where there are relatively small amounts of energy stored in the inductance, but it is impossible to give any general rule as small changes in the circuits influence it considerably. Occasionally discharges are obtained in which it appears that the transfer will be in one direction at one portion of the contacting surfaces and in the opposite direction elsewhere. It is of course conceivable that such reversals might occur if the polarity of the electrodes changed momentarily due to oscillations in the circuit. Such an explanation seems to be ruled out by the fact that the behavior is so radically altered by merely changing the composition of the contacts.

The fact remains however that it is a definite and from a practical viewpoint, an important phenomenon.

The photomicrographs in Fig. 6 illustrate this behavior with pure gold on a circuit of 50 volts interrupting $\frac{1}{6}$ amp. with an inductance of about 1 henry. The cathode has a large accretion from the anode which is deeply eroded over a large portion of its surface. Both surfaces have a dull, mat appearance with more or less brownish discoloration around the edges.

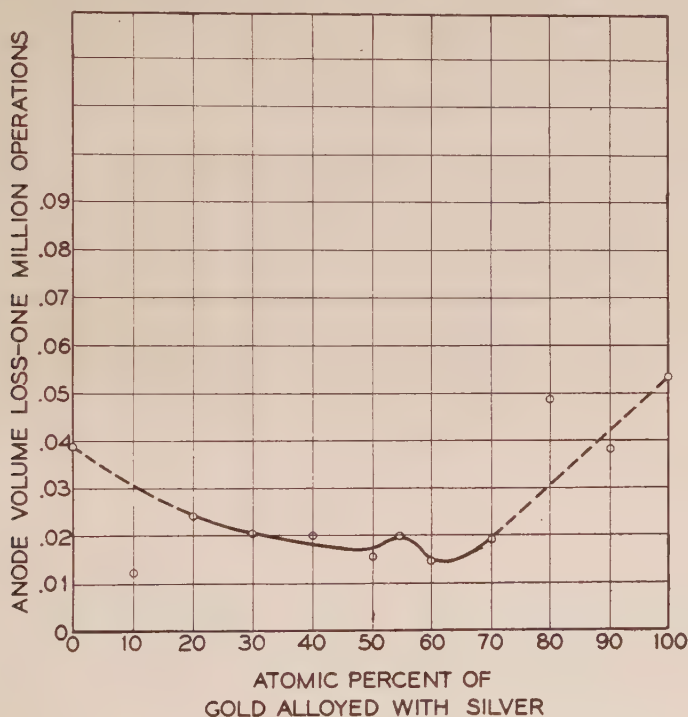


FIG. 7.—VOLUME LOSS OF ANODE OF GOLD-SILVER ALLOYS IN AN INDUCTIVE DISCHARGE.

Fig. 7 shows a typical result for the gold-silver alloys on a circuit of 50 volts interrupting about $\frac{1}{6}$ amp. with an iron core inductance in the circuit of about 1 henry. The figure shows the anode loss instead of the cathode loss shown heretofore. The shape of the curve on the gold side is similar to the one shown previously in Fig. 4. At the opposite end, however, there is only a small rise to the value of silver which is less than that of gold. The particular shape is not the same for various binary series; an anode loss may change to a gain and the curve cross the axis, while with some, the cathode may consistently show the predominating loss as in the preceding examples.

THIRD TYPE OF EROSION—CAPACITY DISCHARGE

In addition to the above two types of erosion associated with the discharges produced on interrupted circuits, there is a third that occurs when closing contacts. The special circuit conditions are illustrated in Fig. 1 inclusive of the capacity and are as follows: If a capacity is shunted across the contacts sufficient to eliminate the glow discharge on interruption, but producing more or less sparking on closure due to the shorting of the capacity, it will be found that, in general, anodes of noble metals will be eroded and the metal will transfer to the cathodes. This direction is the same as in the second type of erosion but the conditions producing it are not the same and the elements have an entirely different order of merit. There is therefore ample justification for considering it a distinct method of erosion.

When a capacity is more or less shorted as occurs in this case there is a current surge which tends to heat and burn out the initial point of contact. This frequently explodes a minute mass of metal and obviously very high temperatures may be attained as contacts are often fused together; in fact it is a well-known method of welding. Assuming there is sufficient force to the relay springs to break the weld, tests show that the cathode picks small particles from the anode, resulting in building up objectionable points so that if the contacts are operating on a very small margin of travel the gap is soon bridged across, with disastrous results to the functioning of the circuit. The effect is therefore of practical interest.

In Table 2 there are given some typical results on a circuit containing 2 microfarads shunted across each contact on a battery of 30 volts. When the circuit is open this shunted capacity will therefore accumulate a charge at 30 volts which will be shorted out as the contacts close. The loss shown in this table is for 1,000,000 operations and the volumes have been obtained by dividing the weight losses in milligrams by the densities of the metals relative to platinum as unity.

TABLE 2.—*Volume Loss of Anode in Capacity Discharge—1,000,000 Operations*

	VOLUME LOSS OF ANODE
A Commercial Alloy of Platinum, Iridium and Rhodium..	3.0
Platinum.....	7.0
Palladium.....	7.2
Gold.....	8.0
Silver.....	10.0

In this table the volume losses decrease as the melting points increase, indicating that the infusibility has some influence and that the erosion could be reduced to a negligible quantity if there were available a material

of sufficiently high fusing temperature. Unfortunately the range is too limited in the more easily available noble metals so that resort must be had, if possible, to protecting the contact by resistance in series with the capacity in order to cut down the current surge on shorting. Alloys even though composed only of the lower melting noble metals apparently have a somewhat reduced loss in comparison with the elements shown in the table but not sufficiently so to offer a solution of the difficulty. In this connection attention should be called to the fact that the platinum-iridium -rhodium alloy which heads the list in Table 2 may for this reason have a somewhat lower loss than would a pure metal of the same melting point.

TRANSFER OF METAL IN DISCHARGES

There have been discussed two factors in contact performance, resistance and erosion, and brief mention has been made of the third, the transfer of material. The material torn off the electrodes may be lost to the side or it may be deposited on the opposite electrode. Discharges between contacts usually take place while the electrodes are very close together so that the conditions are favorable for the retention of free particles. There is of course a certain amount which is lost, the percentage depending on the separation, the shape of the electrodes and the location of the discharge.

It has been found that much of this loose material especially in the glow discharge first appears detached in the form of oxides and possibly other compounds although there may be many points and particles torn off in the form of metal. With the noble metals much of this loosened material often forms a perfectly solid and mechanically strong accretion on one of the electrodes. Some will of course accumulate around the edges where there is no chance for fusion with the body of the electrode. Base metals in general do not build up to anything like the same extent the noble metals as; in fact there is apt to be a small loss where a noble metal would show a gain. Furthermore, in hydrogen the base elements build up more than in air, indicating that a strong reducing atmosphere favors it. This would follow if the phenomenon was dependent on dissociation of the oxides.

It is well known that the oxides of the noble metals are much easier to reduce by heat than are those of the base metals. The temperatures attained by loose particles in the discharge must be exceedingly variable but a microscopic examination indicates that in many cases they are severely heated especially if they tend to form films and loose deposits whose thermal conduction to the body of the electrode is very poor. At the same time these projections and irregularities intensify the field in their neighborhood so that there is a concentration of the discharge on them. This dissociation is very fortunate from the standpoint of keeping

down the oxide and contact resistance in noble metal contacts although at the same time it aids in the building up of objectionable formations of metal.

ACKNOWLEDGMENTS

An attempt has been made in this paper to give an elementary outline of the rather complicated behavior of noble metals as electrical contacts in circuits of special interest to communication engineering. The conditions under which such tests must be carried out to be of practical value, introduce at the same time a number of variables which make the work difficult from a scientific standpoint. Much of the data is of necessity highly statistical, concerning which it is difficult to generalize. Care has been taken to present only those conclusions which have been more definitely established and it is hoped that they will be a distinct contribution to a subject concerning which practically nothing has been written. In conclusion the writer wishes to acknowledge his indebtedness to his colleagues for valuable assistance and advice, especially to Dr. H. E. Ives under whose general supervision the work was conducted, to J. R. Irwin for the results of his practical experience and to H. T. Reeve and H. Boving who prepared most of the alloys and gave valuable metallurgical advice.

DISCUSSION

F. E. CARTER, Newark, N. J.—It is surprising that so little work has been published on the subject of electrical contacts when one considers how much depends on them. The trouble is, of course, that there are so many factors at work in a circuit it is very difficult to predicate just what is going to happen under special conditions. An apparently slight change in a circuit will increase or decrease the electrode loss very considerably indeed. We have carried on a great many experiments on contacts, but not quite along the line that has just been given, because we work with much higher amperage and lower inductance. We find things are very different from what are given in this paper when you get to higher currents. Apparently the condition is reversed; for instance, in Fig. 5 silver is given less than platinum and the statement made that the limiting current for the five metals falls in the order of the melting points. I wonder whether that should not be the vapor tension. Since vapor tension does not altogether fall in the line with melting point, is it not more accurate to say in the order of the vapor pressure? For higher currents, silver with a very much higher vapor tension and lower melting point actually loses less weight than does platinum, showing that other factors are at work.

Concerning the variable resistance of silver, we have shown that that is only too true, although we do not find that the silver oxide film has such a high resistance as is indicated in the paper. It is very variable, but is usually below the platinum-iridium contact resistance, although it may be higher in some cases.

As to erosion in bases other than air, we have done no work with platinum other than to try the effect of oil and gasoline on contacts. Iridium-platinum points are ruined particularly by gasoline. If you drop a little gasoline on a contact point in a magneto, for instance, platinum-iridium points do not last any time at all. Oil is

not quite so bad, but it is serious enough. It is different from tungsten. For tungsten, I understand, it is actually recommended that oil be put on the points, possibly due to the resulting reducing condition.

The curve in Figs. 3 and 4 are very interesting as showing a maximum in the center. I have no explanation to offer for it. It might be correlated somewhat to grain size, and I think Mr. Kingsbury might examine the actual grain size in the alloys just around that point and see whether there is an increase in grain size. Certainly, we know that in a magneto contact structure has a great deal to do with erosion. An iridium-platinum rod, for instance, erodes much less than an iridium-platinum sheet. I mean that if we take a sheet and blank the contact out of it, it does not last nearly as well as if cut from rod.

Mr. Kingsbury indicates that somehow there is a different style of erosion on the anode and the cathode; however, you can make a test run with a magneto and for part of the time the cathode will be built up, and then of its own accord the anode will start to build up. It is very difficult to give any theory for an inversion like that.

The size of gap is the all important thing in contact work. If we get too large or too small a gap, the erosion increases. Mr. Kingsbury, just what success have you had with the oscillograph in determining the current characteristics when the circuit is made and broken, and have you had any experience with the use of two contacts of different materials, one for the anode and one for the cathode? It seems possible the alloy could be varied to suit the erosion for these small currents.

E. WICHERS, Washington, D. C.—Fig. 5 would indicate a relatively small difference in value between platinum and 25 per cent. iridium-platinum. Is that borne out by the facts? We were always led to believe 25 per cent. iridium-platinum was very much superior to soft platinum for contact points.

Relative to the other point to which Dr. Carter just referred, the difference in behavior between contact points cut from rod and punched from sheet: I have heard a good deal about that and wondered whether Mr. Kingsbury also has any information on it.

E. F. KINGSBURY.—My results show the actual disintegration as we have secured it. There is not much difference in the limiting current between the 25 per cent. iridium and platinum itself. This is however consistent with the fact that there is not a large increase in the current even with tungsten whose melting point is considerably greater than the 25 per cent. iridium alloy with platinum.

The point has been raised covering the association of the melting points with some of the characteristics. The evidence indicates that there is a correspondence in some cases although offhand it is not obvious why there should be. It should be kept in mind that when the metal at the point of contact melts the shape of the contacting area may become very unstable. This in turn is likely to cause excessive heating at that point which will explode and volatilize the material. The result would be that the attainment of the melting point would produce a discontinuity in the performance of the contact. This might explain why the characteristics in some cases seem to be determined by the melting point. There are some apparent exceptions which appear to depend on the condition of the surface.

Concerning the use of contacts of dissimilar metals, I infer Dr. Carter means, for example, the use of platinum on one side and a gold-silver alloy on the other. Such an arrangement cannot be used in general because the polarity of the contacts cannot be predetermined. Furthermore, there are many circuits in which it cannot be readily determined which electrode is likely to suffer the most erosion. With dissimilar contacts the material that is eroded most readily will transfer to the opposing electrode and the contacting performance will then be largely determined by that one material.

We have made oscillographic studies of the currents through the contacts and the contact discharges in some typical circuits but perhaps not as completely as you have in mind.

C. S. BRAININ, New York, N. Y.—We have found a great difference in the action of the contact points where the contact is very gentle. We have found that pure platinum sometimes gives better results than platinum iridium. We have also found that a tungsten to silver contact, that is one between two dissimilar metals, under certain circumstances is very satisfactory. Some of the experiments that have been spoken of today are made in magneto tests in which the contact action is quite the reverse of gentle. It is a tapping action. Where the strong tapping action is not present, there is a very different life for contacts than in this instance.

C. G. FINK, New York, N. Y.—Mr. Kingsbury insists on coming back to the interrelation between contact life and melting point. I think Mr. Carter is nearer right when he says we are really dealing with other phenomena beside the melting point.

There is another point: I see that Mr. Kingsbury tried to introduce other properties, such as hardness and life of contact. I think it might be well to study other properties besides; for instance, vapor tension. I think the vapor tension curve of the gold-silver might be very near to the contact life curve. Of course, advantage of tungsten contacts is a high vapor tension. It is true there are little globules of molten metal and it is impossible to tell what will happen, whether they are going to be pinched off or thrown out and so on. Undoubtedly, the vapor tension is a much more important factor than the melting point and some of the other factors.

INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the titles of papers in *italics*.)

A

Admiralty nickel. *See* Adnic.

Adnic, composition and development work, 503

Alclad, aluminum alloy, 125

ALEXANDER, J.: *Discussions; on Grain Growth in Metals Caused by Diffusion*, 397
on Interatomic Forces in Metals and Alloys, 424

Alloys (*See also* constituent metals and trade names):

compressibility, 412, 423

hardness and internal pressures, 417, 422

interatomic forces, 405

secondary. *See* Secondary Metals

soft, secondary recovery, shapes, 708

Alpha Phase Boundary of the Copper-nickel-tin System (PRICE, GRANT AND PHILLIPS), 503

Alterthum method of making metallic single crystals by recrystallization in solid state, 313

Aluminum: annealing, 132

cold forming, 135

commercial: corrosion, fatigue and corrosion-fatigue, 597, 610, 615

X constituent, 193, 195

commercial forms and applications, 99

commercial manipulation, 127

commercial products, list with sizes, 105

commercially pure: definition, 100, 101

hardness, 100, 101

tensile properties, 100, 101, 102

(2S), uses, 100, 101, 104

determination in brass by spectrum analysis, 299

economical properties, 100

effect in brass, 299

hot forming, 138

machining, 149

melting, fluxes, 733

primary production in United States in years 1913-25, 727

riveting, 147

secondary. *See* Aluminum, Secondary.

soldering, 139

special products, 125

tensile strength, 100, 101, 102

welding, 140, 148

Aluminum alloys (*See also* Aluminum-copper, Aluminum-iron-copper, Aluminum-manganese, etc.):

Alclad, 125

Aluminum alloys: annealing, 132

castings, 115

cold forming, 135

commercial forms and applications, 99

commercial products, list with sizes, 105

effect of manganese, 500

fatigue, 609

forging, 124

hardness of cast, 117, 122

hardness, of heat-treated, 127, 128

hot forming, 138

machinability, 158

machining, 149

property of specific lightness, 99

riveting, 147

soldering, 139

special products, 125

strong. *See* Aluminum Strong Alloys

tensile properties, of cast, 117, 122

of heat-treated, 127, 128

3S, properties, 103, 104

uses, 103, 104

welding, 140, 148

Y alloy, castings, 120

commercial forms, 113

Aluminum-beryllium Alloys (ARCHER AND FINK), 616

constitution diagram, 619

revised, 627

corrosion, 641

density, 636

expansion coefficients, 621

hardness, 621 et seq.

literature, 619

microstructure, 628

modulus of elasticity, 646

patents, 620

properties, 618

tensile properties, 621 et seq.

Aluminum-beryllium-copper alloys: corrosion, 641

hardness, 637, 640

tensile strength, 640

Aluminum-bronze: compressibility, 412

fatigue and corrosion-fatigue, 592

Aluminum cable, 125

Aluminum-copper alloy. *See* Aluminum-bronze.

Aluminum-iron-silicon alloys: Chinese script formation, 193, 194

constitution, 179

Guertler method of mapping, 182, 195, 197

unknown phases α (Fe-Si) and β (Fe-Si), 186,

194, 196, 197

- Aluminum-magnesium alloys, 414
- Aluminum-manganese alloys:
fatigue and corrosion-fatigue, 599
3S, properties, 103, 104
uses, 103, 104
- Aluminum scrap, drosses and skims, sampling
and evaluating, 680, 734
market prices, 729
- Aluminum, secondary: evaluation of scrap, 737
ingots, 707
market prices, 729
recovery in United States, in 1913-25, 727
in 1924-25, 695
in 1925, 701
in 1910-26, 663 et seq.
remelting, 726
sources, 727
types, 727
- Aluminum-silicon alloys: castings, 119
commercial use, 198, 203
constitution, 201
effect on machining of high-temperature
anneal followed by a draw, 227
hardness: of cast, 209, 211, 213, 220, 221
of forged, 206
heat-treatment investigation, 198, 203
modified, 202, 204
normal, 202
precipitation hardening, 222
solubility equilibria, 164
tensile properties: of cast, 209, 211, 213, 220,
221
of forged, 206
- Aluminum strong alloys: commercial forms, 113
description, 108
heat treatment, 108
hot-pressing, 112
nominal compositions, 110
strength, ductility and corrosion resistance,
110, 111
tensile properties, 109
- Aluminum-zinc-copper-iron alloy, castings, 120
- ANDERSON, H. A.: *Discussion on Equilibrium
Relations in Aluminum-silicon and
Aluminum-iron-silicon Alloys of
High Purity*, 196
- Annealing: aluminum and its alloys, 132
monel metal and nickel, 76, 84
sterling silver, 746, 756, 758
- Antimony: determination in tin by spectrum
analysis, 299
in ternary diagrams, 316
- Antimony, secondary: recovery in United States,
in 1910-26, 663 et seq.
in 1924-25, 695
in 1925, 701
- Antimony-lead alloys. *See* Lead-antimony
- Application of a High-vacuum Induction Furnace
to the Study of Gases in Metals* (BRACE
AND ZIEGLER) 544
- ARCHER, R. S.: *Discussion on Heat Treatment of
Aluminum-silicon Alloys*, 227
- ARCHER, R. S. AND FINK, W. L.: *Aluminum-
beryllium Alloys*, 616; *Discussion*, 646
- ARCHER, R. S., KEMPF, L. W. AND HOBBS, D. B.:
*Heat Treatment of Aluminum-silicon
Alloys*, 198
- ARMSTRONG, P. A. E.: *Discussion on Grain on
Growth in Metals Caused by Diffusion*,
399
- Arnold bending test, 61
- Arsenic, determination in copper by spectrum
analysis, 296
- B
- Babbitt, lead content limit, 717, 719
- BALUT, S. J.: *Discussion on The Platinum Metals
and Their Alloys*, 785
- BASSETT, W. H.: *Discussions: on Distribution of
Tensile Strength in Hard Drawn
Copper Wire*, 541
*on Physical Characteristics of Com-
mercial Copper-zinc Alloys*, 72, 73
- BASSETT, W. H. AND DAVIS, C. H.: *Physical
Characteristics of Commercial Copper-
zinc Alloys*, 55
- Battery plates, sampling and evaluating, 681, 691
- Behavior of Molybdenum as Resistor in the Electric
Furnace* (MILLER AND LINDEMAN)
647
- Bending test, machine for, 61
- BENEDICKS, C.: *Discussions: on Grain Growth in
Metals Caused by Diffusion*, 402
on Twinning in Copper and Brass, 441
- Benedicks method of determining twinning in
metals, 441
- Benzol poisoning, control by spectrum analysis
of air, 306
- Beryllium: commercial, modulus of elasticity, 646
density, 643
electrical resistivity, 643
properties, 617
- Bibliography: lead-tin-cadmium alloys as solders,
361
spectrum analysis, 303
- Bismuth: determination in copper by spectrum
analysis, 296
determination in lead by spectrum analysis,
300
effect in solder, 356
in ternary diagrams, 316
- BLACKMAR, D. C.: *Modern Non-ferrous Secondary
Metal Producer*, 700
- BRACE, P. H. AND ZIEGLER, N. A.: *Application of
a High-vacuum Induction Furnace to
the Study of Gases in Metals*, 544;
Discussion, 570
- BRAININ, C. S.: *Discussion on Use of the Noble
Metals for Electrical Contacts*, 824
- Brass, secondary: ingots, 705
recovery in United States, in 1910-26, 663
in 1914-25, 695
- Brass (*See also* Copper-zinc Alloys):
compressibility, 414
determination of aluminum by spectrum
analysis, 299
effect of aluminum, 299
grain size effect on surface, 69, 71

- Brass: physical properties, 58
 recrystallized, nature of bands, 430
 sheet, specification essentials, 69
- Brass scrap: exported, 1925-26, 664
 specifications of Ohio Brass Company, 718
 yellow, classifications, 703
- Brass skimmings, sampling and evaluating, 680
- Brazing: monel metal and nickel, 87
- British Non-ferrous Metals Research Assn.,
 quantitative spectrum analyses, 292
- Bronze. *See* Copper-zinc-alloys and Manganese-bronze
- Bronze, secondary: ingots, 705
 recovery from foundry slags, 721
- BROWN, W. J.: *Discussion on Sampling and Evaluating Secondary Non-ferrous Metals*, 689
- BUERGER, M. J.: *The Cause of Translation Striae and Translation Strain-hardening in Crystals*, 375
- BURROWS, H. O., STAY, T. D. AND HOBBS, D. B.:
Remelting Secondary Aluminum, 726
- C
- Cable: aluminum, 125
 lead-covered, scrap, sampling and evaluating, 685
- Cadmium: determination in zinc by spectrum analysis, 292
 effect in solders, 352, 362, 367
- Cadmium-zinc alloys as solders, 365
- Calcium, determination in magnesium by spectrum analysis, 298
- CAMP, A. D.: *Discussion on Some Aspects of the Commercial Manipulation of Aluminum*, 148
- CAMPBELL, W.: *Discussion on Ternary Systems of Lead-antimony and a Third Constituent*, 348
- CAPILLON, E. A.: *Discussions: on Gold, Silver, Copper Alloys*, 803
on Manufacture of Sterling Silver and Some of Its Physical Properties, 757
on The Platinum Metals and Their Alloys, 782
- Carbon, determination in steel by spectrum analysis, 301
- CARTER, F. E.: *Gold, Silver, Copper Alloys*, 786
The Platinum Metals and Their Alloys, 759;
Discussion, 782, 783, 785
Discussions: on Distribution of Tensile Strength in Hard Drawn Copper Wire, 540
on Manufacture of Sterling Silver and Some of Its Physical Properties, 757
on Use of the Noble Metals for Electrical Contacts, 822
- Casting: aluminum alloys, 115
 monel metal and nickel, 85
 sterling silver, 745
- Castings: monel metal and nickel, types that can be purchased, 93
- Cause of Translation Striae and Translation Strain-hardening in Crystals* (BUERGER) 375
- CHARTKOFF, E. P.: *Discussion on Condition of Thorium in Thoriated Tungsten Filament*, 238
- CHATFIELD, C. H. AND LEACH, R. H.: *Manufacture of Sterling Silver and Some of Its Physical Properties*, 743
- Chinese script formation. *See* Aluminum-iron-silicon alloys
- Chromium: determination in steel, by spectrum analysis, 300, 303, 305
 diffusion in iron, grain growth, 392, 400
- CLAMER, G. H.: *Discussions: on Metal Recovery from Bronze Foundry Slags*, 724, 725
on Modern Non-ferrous Secondary Metal Producer, 709
- CLARK, F. H.: *Discussions: on Distribution of Tensile Strength in Hard Drawn Copper Wire*, 536
on A Study of Certain Alloys of the Lead-tin cadmium System with Reference to Their Use as Solders, 367
- Classification and Preparation of Non-ferrous Scrap Metals and Alloys* (SIEFERT) 694
- COLCORD, F. F.: *Discussions: on Sampling and Evaluating Secondary Non-ferrous Metals*, 692
on A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders, 367
- Commercial Forms and Applications of Aluminum and Aluminum Alloys* (FARAGHER) 99
- Compressibility (See also names of metals and alloys): as measure of hardness, 425, 427, 428
 as measure of interatomic force in metals, 411
 compared with hardness, 408
- Condition of Thorium in Thoriated Tungsten Filament* (ST. JOHN) 228
- Contacts. *See* Electrical Contacts
- Contamination of Metal Scrap, Its Effect on the Value, and Suggested Means of Control* (THIEME) 711
- Copper: determination in lead by spectrum analysis, 300
 determination of bismuth and arsenic by spectrum analysis, 296, 297
 fatigue and corrosion-fatigue, 596
 in ternary diagrams, 316
 manganese as scavenger, 483
 overpooled, research suggested on occluded gas, 566
 recrystallized, nature of bands, 430
 structure of cracks caused by repeated stress, 536
 tensile strength, elongation and grain size, comparison of lake and electrolytic, 57
- Copper scrap: exported, 1925-26, 664
 sampling and evaluating, 689
- Copper, secondary: ingots, 705
 recovery in United States in 1910-26, 663
 in 1924-25, 695
 in 1925, 701
 in 1925-26, 664
- Copper skimmings, sampling and evaluating, 680

- Copper wire, hard drawn: brittleness, "cup and cone," 519, 536, 540
 laminations, cause and detection, 518
 microstructure, 531
 tensile strength: dependent on diameter, 521
 distribution, 518
 effect of bending, 521, 529
 effect of internal strains, 540, 542
 effect of reversal of drawing direction, 530
 effect of self-annealing, 540, 541
 effect of successive drafts, 527
 skin-hardness theory, 521
- Copper-aluminum alloy, compressibility, 412
- Copper-gold alloys, hardness and internal pressures, 417
- Copper-manganese alloys: ductility, 485
 electrical resistivity, 488
 equilibrium diagram, 484
 hardness, 486
 industrial uses, 485, 488, 491
 melting point, 491
 rolling and drawing properties, 490
 tensile strength, 487
 ternary, properties, 491
- Copper-manganese-aluminum alloys: Heusler bronzes, 498
 properties, 491
- Copper-manganese-silicon alloys, properties, 491
- Copper-manganese-tin alloys, properties, 491
- Copper-manganese-zinc alloys, properties, 491
- Copper-nickel alloys: compressibility, 412
 hardness and internal pressure, 417
- Copper-nickel-tin alloys: alpha phase boundary, 503
 equilibrium diagram, 515
 hardening, 511
 hardness in various conditions, 515
 tensile properties, 515
- Copper-tin alloys, compressibility, 414
- Copper-zinc alloys: bending tests, 61
 commercial, physical characteristics, 55
 compressibility, 412
 grain growth during heat treatment, 68
 growth of the metallography, 55
 hardness increase with variation of copper content and cold rolling, 63
 literature, 55
 structure change during heat treatment, 65
 tensile properties, 58, 72
- Corrosion: aluminum-beryllium alloys, effect on tensile properties, 645
 aluminum strong alloys, 111
 salt-spray tests on aluminum-beryllium alloys, 641
- Corrosion-fatigue (*See also* names of metals):
 compared with fatigue in commercially pure aluminum, 610, 615
 definition, 571
 effect of shape of corrosion notch, 601, 609, 610, 613
 ferrous alloys, effect of absorption of hydrogen, 611, 614
 limit, definition, 571
- Corrosion-fatigue: prior-corrosion fatigue, definition, 571
 importance, 610
 process, 571
 stages, 571
- Corrosion of Metals as Affected by Time and by Cyclic Stress* (McADAM) 571
- CORSE, W. M.: *Discussion on Contamination of Metal Scrap*, 718
- CORSON, M. G.: *Manganese in Non-ferrous Alloys*, 483
- COWAN, W. A.: *Discussion on Contamination of Metal Scrap*, 720
- CRAMPTON, D. K.: *Discussions: on Distribution of Tensile Strength in Hard Drawn Copper Wire*, 540
 on Physical Characteristics of Commercial Copper-zinc Alloys, 72
- CRAWFORD, C. A.: *Nickel and Monel Metal, with Especial Reference to Annealing*, 74
- Crystals, aluminum twinning doubtful, 13, 16
- Crystals, antimony: lattice form, 19
 twinning plane and axis, 19
- Crystals, beryllium: axial ratio, 19, 445
 lattice constants, 445
 twinning: after deformation, 446
 plane and axis, 19, 445
- Crystals, bismuth: lattice form, 19
 twinning plane and axis, 19
- Crystals, brass, twinning, 8, 33, 429
- Crystals, cadmium: axial ratio, 19, 445
 lattice constants, 445
 twinning: after deformation, 446
 plane and axis, 19, 445
- Crystals, calcium, twinning, no data, 16
- Crystals, cerium: axial ratio, 19
 twinning, 16
- Crystals, chromium, twinning, no data, 18
- Crystals, cobalt: axial ratio, 19
 twinning, 16
- Crystals, copper: twinning, 8, 20, 36, 429, 439
 literature, 429
 plane and axis, 16
- Crystals, ferrite: goniometer method of study, 453, 459
 Neumann bands, 11
 twin-boundary stability, 459
 twinning, 10, 453
- Crystals, germanium, lattice form, 19
- Crystals, gold, twinning plane and axis, 16
- Crystals, hafnium, axial ratio, 19
- Crystals, indium: lattice form, 19
 twinning plane, 19
- Crystals, iridium, twinning plane and axis, 16
- Crystals, iron: Neumann bands, 11
 twinning, 10
 plane, axis (alpha), 18
 plane, axis (gamma), 16
 twinning and recrystallization in hammered iron, 20, 33
- Crystals, lead: twinning, mode of occurrence, 15
 plane and axis, 16
- Crystals, lithium, twinning, no data, 18

- Crystals, magnesium (*See also* Magnesium, etching and microstructure): axial ratio, 445, 19
lattice constants, 445
twinning: after deformation, 446
plane and axis, 19, 445
- Crystals, metallic: goniometer method of study, 453, 459
recrystallization in wrought metals, 20
single: method of production, 307, 314
translation striae and strain-hardening, cause, 375
slip in plastic deformation, 46
twinning: and slip in plastic deformation, 46, 53
Benedick's method of determining, 441
body-centered cubic metals, 18
can be proved without X-ray, 460
distortion at twin boundaries, 40
face-centered cubic metals, 16
hexagonal close-packed metals, 19
in wrought metals, 20
survey of subject, 7
- Crystals, molybdenum, twinning, no data, 18
- Crystals, nickel, twinning, 15
- Crystals, osmium, axial ratio, 19
- Crystals, palladium, twinning, no data, 16
- Crystals, platinum, twinning plane and axis, 16
- Crystals, potassium, twinning, no data, 18
- Crystals, rhodium, twinning, no data, 16
- Crystals, ruthenium, axial ratio, 19
- Crystals, silver, twinning plane and axis, 16
- Crystals, sodium, twinning, no data, 18
- Crystals, steel, twinning, 10
- Crystals, tantalum, twinning, no data, 18
- Crystals, tellurium, lattice form, 19
- Crystals, thorium, twinning, no data, 16
- Crystals, tin: (gray), lattice form, 19
twinning, 13
(white), lattice form, 19
(white), twinning plane and axis, 19
- Crystals, titanium, axial ratio, 19
- Crystals, tungsten, twinning, no data, 18
- Crystals, vanadium, twinning plane and axis, 18
- Crystals, zinc: axial ratio, 19, 269, 445
condition during deformation, 242
lattice constants, 445
plastic deformation, evidence of twinning, 269, 273, 276
plastic deformation of polycrystalline strip, X-ray analysis, 242, 246, 272, 276
single, fracture, X-ray analysis, 264
single, plastic deformation, X-ray analysis, 253, 273, 276
twinning and recrystallization in rolled zinc, 20, 21
after plastic deformation, 241, 269, 272, 273, 276
hypothesis, 250, 272, 276
mode of occurrence, 13
plane and axis, 19, 445
- Crystals, zirconium, axial ratio, 19
- Cupronickel, fatigue and corrosion-fatigue, 596
- Czochralski method of making metallic single crystals, 308, 314
- D
- DALBEY, G. E.: *Discussions: on A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 362, 367
on Some Peculiar Results in Hardness Tests of Lead-antimony Alloys, 374
- DALZELL, R. C.: *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 569
- DARBY, E. R.: *Metal Recovery from Bronze Foundry Slags*, 721; *Discussion*, 724, 725
Discussions: on Contamination, of Metal Scrap, 719
on Modern Non-ferrous Secondary Metal Producer, 709
- DAVIS, C. H. AND BASSETT, W. H.: *Physical Characteristics of Commercial Copper-zinc Alloys*, 55
- DAVIS, C. H.: *Discussion on Physical Characteristics of Commercial Copper-zinc Alloys*, 71
- DEAN, R. S.: *Discussions: on A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 366, 367
on Some Peculiar Results in Hardness Tests of Lead-antimony Alloys, 373, 374
on Ternary Systems of Lead-antimony and a Third Constituent, 351
- Deformation of metals. *See* Plastic Deformation
- DELASZLO, H. G.: *Discussion on Quantitative Spectrum Analysis*, 305
- Diffraction, X-ray. *See* X-ray.
- Diffusion: definition of "force of diffusion," 393, 402, 403
in metals, columnarisation, 392, 396, 399
of metals: effect on grain growth, 390
in iron, grain growth, 390, 396, 400, 402
possibility of shrinking membrane, 399
work by Grube in Germany, 395
- Distribution of Tensile Strength in Hard Drawn Copper Wire* (HARRIS) 518
- DIX, E. H. JR.: *Discussion on Alpha Phase Boundary of the Copper-nickel-tin System*, 517
- DIX, E. H. JR., AND HEATH, A. C. JR.: *Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity*, 164
Discussion on Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity, 196
- DIX, E. H. JR. AND KEITH, W. D.: *Discussion on Manganese in Non-ferrous Alloys*, 502
- DOAN, G. E.: *Discussion on Interatomic Forces in Metals and Alloys*, 422
- Drawing: monel metal and nickel, 86
zinc, directions, 98
- DUNLOP, J. P.: *Non-ferrous, Secondary Metals Recovered in the United States*, 660; *Discussion*, 671

- Duralumin (*See also* Aluminum strong alloys):
 corrosion, 110, 111, 599
 corrosion-fatigue, 599
 ductility, 110, 111
 fatigue, 609, 614
 hardness, 109, 127, 128
 heat-treating, 127
 manganese content, 500
 nominal composition, 110
 tensile properties, 109, 127, 128
- E
- EDWARDS, F. H.: *Discussion of A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 366
- EGERBERG, B.: *Discussion on Manufacture of Sterling Silver and Some of Its Physical Properties*, 757
- ELAM, C. F.: *Discussions: on Twinning in Copper and Brass*, 440
on Twinning in Ferrite, 460
- Electrical contacts: dissimilar metals, 823
 erosion of electrodes, 808
 of noble metals, 804
 research needed, 804
- ELLIS, O. W.: *Discussions: on Contamination of Metal Scrap*, 719
on Manufacture of Sterling Silver and Some of Its Physical Properties, 755
on A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders, 367
- Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity* (DIX AND HEATH), 164
- Erosion of electrodes. *See* Electrical Contacts
- F
- FARAGHER, P. V.: *Commercial Forms and Applications of Aluminum and Aluminum Alloys*, 99
Discussion on Some Aspects of the Commercial Manipulation of Aluminum, 148
- Fatigue. *See* Corrosion—fatigue and names of metals
- FELL, E. W.: *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 566
 high-frequency induction vacuum furnace, 566
- Ferrite crystals. *See* Crystals, Ferrite
- FINK, C. G.: *Discussion on Use of Noble Metals for Electrical Contacts*, 824
- FINK, W. L. AND ARCHER, R. S.: *Aluminum beryllium Alloys*, 616; *Discussion*, 646
- FITZPATRICK, E.: *Discussion on Sampling and Evaluating Secondary Non-ferrous Metals*, 691, 692, 693
- Forging monel metal and nickel, 85
- Forgings: aluminum alloy, 124
 monel metal and nickel, types that can be purchased, 93
- FULLER, T. S.: *Discussions: on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 610
on Grain Growth in Metals Caused by Diffusion, 396
- Furnace: electric, molybdenum as resistor, 647
 high-vacuum induction, for study of gases in metals, 544, 566
- G
- GANN, J. A.: *Discussion on Magnesium—Its Etching and Structure*, 477
- Gases: from iron, Armco, 559, 565
 electrolytic, 559
 in metals: determination, 557, 564
 determination in overpoled copper needed, 566
 study with high-vacuum induction furnace, 544, 566
 solubility in iron, theory, 561
- Gasoline, estimation of tetraethyl lead by spectrum analysis, 306
- GILLETT, H. W.: *Discussions: on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 609
on Interatomic Forces in Metals and Alloys, 420
- Gold alloys, etching reagent, 802
Gold, Silver, Copper Alloys (CARTER), 786
- Gold-silver-copper alloys: etching reagent, 802
 10-kt., hardness variation, 802
 14-kt., properties, 786 et seq.
 18-kt., properties, 795 et seq.
- GRAHAM, W. F.: *Discussions: on Contamination of Metal Scrap*, 717
on Metal Recovery from Bronze Foundry Slages, 724, 725
- Grain growth: copper-zinc alloys, during heat treatment, 68
 in metals, caused by diffusion, 390
- Grain Growth in Metals Caused by Diffusion* (KELLEY), 390
- GRANT, C. G., PRICE, W. B. AND PHILLIPS, A. J.: *Alpha Phase Boundary of the Copper-nickel-tin System*, 503
- GREGG, J. L.: *Discussion on Interatomic Forces in Metals and Alloys*, 425
- GRUBE, G.: *diffusion of metals*, 395
- GRUNER, J. W.: *Discussion on The Cause of Translation Striae and Translation Strain-hardening in Crystals*, 388
- Guertler method of mapping ternary diagrams applied to Al-Fe-Si system, 182, 195, 197
- H
- Hand-hammering monel metal and nickel, 86
- HARDER, O. E.: *Discussion on Twinning in Ferrite*, 460
- HARDNESS (*See also* names of metals and alloys):
 compared with compressibility, 408
 comparison of value of several measuring systems and suggestion of research on elastic hardness, 424, 427
 factors governing, 409, 421, 422

- HARDNESS:** in terms of compressibility and internal pressures, 417, 422, 425, 427, 428
slip-interference theory vs. compressibility, 421
- HARRIS, F. W.:** *Distribution of Tensile Strength in Hard Drawn Copper Wire*, 518;
Discussion, 540, 541, 543
- Heat treatment:** aluminum alloys, 127, 198
aluminum castings, 119
aluminum strong alloys, 108
- Heat Treatment of Aluminum-silicon Alloys** (ARCHER, KEMPF AND HOBBS) 198
- HEATH, A. C. JR.:** *Discussion on Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity*, 196
- HEATH, A. C. JR., AND DIX, E. H. JR.:** *Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity*, 164
- HESSENBRUCH, W.:** *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 567
- Heusler bronzes**, 498
- HIDNERT, P. AND SWEENEY, W. T.:** *Discussion on Aluminum-Beryllium Alloys*, 643
- HIERS, G. O.:** *Discussions: on Some Peculiar Results in Hardness Tests of Lead-antimony Alloys*, 373, 374
on Ternary Systems of Lead-Antimony and a Third Constituent, 351
- HIRSCH, W. C.:** *Discussions: on Modern Non-ferrous Secondary Metals Producer*, 710
on Non-ferrous Secondary Metals Recovered in the United States, 669
- HOBBS, D. B., ARCHER, R. S. AND KEMPF, L. W.:** *Heat Treatment of Aluminum-silicon Alloys*, 198
- HOBBS, D. B., STAY, T. D. AND BURROWS, H. O.:** *Remelting Secondary Aluminum*, 726
- HOWARD, L. O.:** *Some Peculiar Results in Hardness Tests of Lead-antimony Alloys*, 369; *Discussion*, 374
- HOYT, S. L.:** *Discussions: on Condition of Thorium in Thoriated Tungsten Filament*, 238
on Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity, 196
on Grain Growth in Metals Caused by Diffusion, 398
on Heat Treatment of Aluminum-silicon Alloys, 227
on Interatomic Forces in Metals and Alloys, 424
on The Production of Metallic Single Crystals, 314
on X-ray Analysis of Plastic Deformation of Zinc, 276
- HOYT, S. L. AND WILSON, T. A.:** *X-ray Analysis of Plastic Deformation of Zinc*, 241
- Interatomic forces in metals and alloys:** expressed as pressures, 408, 416
measured by compressibility, 411
- Interatomic Forces in Metals and Alloys** (MEHL) 405
- Invar**, compressibility, 412
- Iridium alloys** (*See also* Platinum-iridium), brief description, 775
- Iron:** Armco, gases from, 559, 565
determination in zinc by spectrum analysis, 292
diffusion of metals in, work by Grube in Germany, 395
electrolytic, gases from, 559
grain growth following diffusion of metals in, 390, 396, 400, 402
solubility of gases in, theory, 561
- Iron crystals.** *See* Crystals, Iron, and Crystals, Ferrite
- Iron-nickel alloy**, compressibility, 412
- Iseki method** of making metallic single crystals, 308

J

- JASPER, T. M.:** *Discussion on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 612
- JEFFRIES, Z.:** *Discussions: on Condition of Thorium in Thoriated Tungsten Filament*, 239
on Grain Growth in Metals Caused by Diffusion, 399
on Interatomic Forces in Metals and Alloys, 424
on Manganese in Non-Ferrous Alloys, 502
on The Production of Metallic Single Crystals, 315
on Twinning in Ferrite, 459
- JORDAN, L. AND VACHER, H. C.:** *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 564

K

- KEITH, W. D. AND DIX, E. H.:** *Discussion on Manganese in Non-Ferrous Alloys*, 502
- KELLEY, F. C.:** *Grain Growth in Metals Caused by Diffusion*, 390
- KEMPF, L. W., ARCHER, R. S. AND HOBBS, D. B.:** *Heat Treatment of Aluminum-silicon Alloys*, 198
- KINGSBURY, E. F.:** *Use of the Noble Metals for Electrical Contacts*, 804; *Discussion*, 823
- Koref method** of making metallic single crystals, 309
- KUNZ, G. F.:** *Discussion on Gold, Silver, Copper Alloys*, 803

L

- Landgraf-Turner alternating bending machine**, 61
- LANE, A. C.:** *Discussion on Twinning in Copper and Brass*, 441
- I**
- Institute of Metals Division, Annual Lecture**, 1928, 7

- LAW, E. H.: *Discussion on Sampling and Evaluating Secondary Non-ferrous Metals*, 689
- LEACH, R. H.: *Discussion on Manufacture of Sterling Silver and Some of Its Physical Properties*, 758
- LEACH, R. H. AND CHATFIELD, C. H.: *Manufacture of Sterling Silver and Some of Its Physical Properties*, 743
- Lead: determination in zinc by spectrum analysis, 292
- determination of impurities by spectrum analysis, 300
- primary, produced in 1925-26 in United States, 665
- tetraethyl, estimation in gasoline by spectrum analysis, 306
- Lead scrap, sampling and evaluating, 681, 690
- Lead, secondary: recovery in United States, in 1910-26, 663
- 1924-25, 695
- 1925, 701
- Lead-antimony alloys: expansion on solidifying, 373
- hardness tests, 369
- literature, 369
- Lead-antimony-bismuth system, investigation, 316, 327
- Lead-antimony-copper system, investigation, 316, 317, 348
- Lead-antimony-tin system, lead corner, 316, 336
- Lead-tin-cadmium alloys: as solders, 352
- freezing points, 362
- Lead-tin-cadmium-zinc alloys: tensile strength, elongation, and reduction of area, 363
- solidification ranges, 356
- LESTER, H. H.: *Discussion on Interatomic Forces in Metals and Alloys*, 421
- LINDEMAN M. AND MILLER, H. J.: *Behavior of Molybdenum as Resistor in the Electric Furnace*, 647
- Lodyguine method of making metallic single crystals, 308
- LUNN, E.: *Discussion on Some Aspects of the Commercial Manipulation of Aluminum*, 148
- M
- Machining Aluminum* (TEMPLE), 149
- Machining monel metal and nickel, 86
- Magnesium: density, 475
- determination of calcium by spectrum analysis, 298
- etching, 461, 471, 478
- etching reagents, 463, 478
- hardness, 475
- microstructure, 464, 477, 478, 482
- Magnesium-aluminum-alloys: density, 476
- effect of manganese, 502
- hardness, 476
- making and use, 500
- microstructure, 476
- structure, 500, 502
- Magnesium—Its Etching and Structure* (PULSIFER) 461
- Manganese: as scavenger in copper, 483
- determination in steel by spectrum analysis, 300
- effect in magnesium-aluminum alloys, 502
- in aluminum alloy, 3 S, 103
- in non-ferrous alloys, 483
- properties, 483
- Manganese in Non-ferrous Alloys* (CORSON) 483
- Manganese-bronzes: constitution, 493
- properties, 498
- Manganese-copper alloys. *See* Copper-manganese
- Manganese-silver alloys, constitution and possible uses, 501
- Manganese-silver-aluminum alloys, properties, 502
- Manufacture of Sterling Silver and Some of Its Physical Properties* (LEACH AND CHATFIELD), 743
- MATHEWSON, C. H., AND PHILLIPS, A. J.: *Twinning in Beryllium, Magnesium, Zinc and Cadmium*, 445
- MATHEWSON, C. H.: *Twinning in Metals*, 7
- Discussion on X-ray Analysis of Plastic Deformation of Zinc*, 272
- McADAM, D. J. JR.: *Corrosion of Metals as Affected by Time and by Cyclic Stress*, 571; *Discussion*, 613
- McKAY, R. J.: *Discussion on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 611
- McKEEHAN, L. W.: *Twinning in Ferrite*, 453; *Discussion*, 460
- Discussions: on Condition of Thorium in Thoriated Tungsten Filament*, 238
- on Grain Growth in Metals Caused by Diffusion*, 398
- on The Production of Metallic Single Crystals*, 314
- on Twinning in Copper and Brass*, 440
- on X-ray analysis of Plastic Deformation of Zinc*, 269, 276
- MEHL, R. F.: *Interatomic Forces in Metals and Alloys*, 405; *Discussion*, 426
- MERICA, P. D.: *Discussions: on Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity*, 194
- on Heat Treatment of Aluminum-silicon Alloys*, 227
- on Physical Characteristics of Commercial Copper-zinc Alloys*, 72
- Metal Recovery from Bronze Foundry Slags* (DARBY) 721
- Metallography of copper-zinc alloys, growth, 55
- Metals (See also names of metals): corrosion as affected by time and cyclic stress, 571
- hardness described in terms of interatomic forces, 410
- interatomic forces, 405
- interatomic forces in relation to hardness, 410
- periodic properties, 406
- solubility of gases in, theory, 561
- specifications should be more widely used, 710

- MILLER, H. J. AND LINDEMAN, M.: *Behavior of Molybdenum as Resistor in the Electric Furnace*, 647
- Modern Non-ferrous Secondary Metal Producer (BLACKMAR) 700
- Molybdenum: as resistor in electric furnace, 647
diffusion in iron, grain growth, 392
- Monel metal: annealing, 76
casting, 85
commercial products, classes, details regarding, 87
commercial products, list, 74
composition, 75
ductility dependent on cold work before annealing, 78
ductility related to grain size, 81
fatigue and corrosion-fatigue, 596
forging, 85
physical properties, 75
working and fabricating (pickling, machining, etc.,) 76
- MOORE, H. F.: *Discussions: on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 609
on Distribution of Tensile Strength in Hard Drawn Copper Wire, 536
- MORGEN, R. A., SWENSON, L. G., NIX, F. C. AND ROBERTS, E. H.: *Ternary Systems of Lead-Antimony and a Third Constituent*, 316
- Muntz metal, fatigue and corrosion-fatigue, 597
- N
- NAGEL, C. F. JR., *Some Aspects of the Commercial Manipulation of Aluminum*, 127
- Neumann bands: in magnesium, 464, 467, 482
mode of occurrence, 11
- Newloy, composition, 503
- Nickel and Monel Metal, with Especial Reference to Annealing (CRAWFORD) 74
- Nickel: annealing, 76
casting, 85
commercial products, classes, details regarding, 87
commercial products, list, 74
determination in steel by spectrum analysis, 303, 305
ductility dependent on cold work before annealing, 78
ductility related to grain size, 81
electrolytic, use, 93
forging, 85
grades, 75
physical properties, 75
working and fabricating (pickling, machining, etc.,) 76
- Nickel, secondary: recovery in United States in 1910-26, 663 et seq.
in 1924-25, 695
- Nickel-copper alloys (See also Monel Metal), fatigue and corrosion-fatigue, 594
- Nickel-silver, secondary production, contamination from poorly sorted scrap, 718
- NIX, F. C., MORGEN, R. A., SWENSON, L. G. AND ROBERTS, E. H.: *Ternary Systems of Lead-antimony and a Third Constituent*, 316
- Noble metals for electrical contacts, 804
- Non-ferrous alloys containing manganese. See Copper-manganese Alloys, Copper-manganese-zinc Alloys, Manganese Bronzes, etc.
- Non-ferrous Secondary Metals Recovered in the United States (DUNLOP) 660
- O
- Orbig. See Schaller
- Osmium alloys, brief description, 775
- P
- Palladent, 785
- Palladium alloys: etching reagent, 802
list with brief description, 775
- Palladium plating, 783, 784
- PEIRCE, W. M.: *Discussion on X-ray Analysis of Plastic Deformation of Zinc*, 274
- PHILLIPS, A. J.: *Twinning in Copper and Brass*, 429; *Discussion*, 443
Discussions: on Alpha Phase Boundary of the Copper-nickel-tin System, 517
on Magnesium—Its Etching and Structure, 482
- PHILLIPS, A. J. AND MATHEWSON, C. H.: *Twinning in Beryllium, Magnesium, Zinc and Cadmium*, 445
- PHILLIPS, A. J., PRICE, W. B. AND GRANT, C. G.: *Alpha Phase Boundary of the Copper-nickel-tin System*, 503
- Physical Characteristics of Commercial Copper-zinc Alloys (BASSETT AND DAVIS) 55
- Pickling monel metal and nickel, 86
- PILLING, N. B.: *Discussion on Twinning in Copper and Brass*, 439
- Plastic deformation: aluminum and its alloys, cold forming, 135
hot forming, 138
metals; cause of translation striae and strain-hardening in crystals, 375
effect of interatomic forces, 405
functions of crystal twinning and slip, 46, 53
zinc. See Zinc
- Platinum alloys: list with brief descriptions, 770
uses in industry, 778
working, 762
- Platinum (See also Platinum Metals) determination in silver by spectrum analysis, 305
effect of graphite mold in casting, 783, 784
metallurgy, 761
ore, places and forms of occurrence, 759
soldering, 762
substitutes for, in electrical contacts, 804
welding, 762
working, 762, 783, 784

- Platinum Metals and Their Alloys* (CARTER) 759
- Platinum metals: metallography, 766
- physical properties, 764
- reaction with gases, 762, 782
- spectrum analysis, quantitative, 766
- Platinum plating, 783, 784
- Platinum-iridium alloys: hardness, ductility and electrical resistance, 772
- oxidation, 783, 784
- use in jewelry, 771
- Platinum-mercury amalgam, 782, 784
- PLUMMER, C. E.: *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 569
- Pressures in metals: as measure of hardness, 425, 427, 428
- expressed as interatomic forces, 416
- Pressures in solids, mode of expressing interatomic forces, 408
- PRICE, W. B.: *Discussion on Corrosion of Metals as Affected by Time and by Cyclic Stress*, 612
- on *Distribution of Tensile Strength in Hard Drawn Copper Wire*, 540, 541
- PRICE, W. B., GRANT, C. G. AND PHILLIPS, A. J.: *Alpha Phase Boundary of the Copper-nickel-tin System*, 503
- Production of Metallic Single Crystals* (VAN LIEMPT) 307
- PULSIFER, H. B.: *Magnesium—Its Etching and Structure*, 461; *Discussion*, 477, 482
- Punching monel metal and nickel, 86
- Q
- Quantitative Spectrum Analysis* (TWYMAN AND SMITH) 280
- R
- RAWDON, H. S.: *Discussion on Aluminum-beryllium Alloys*, 644
- on *Corrosion of Metals as Affected by Time and by Cyclic Stress*, 608
- REEVE, H. T.: *Discussion on The Platinum Metals and Their Alloys*, 783
- Remelting Secondary Aluminum* (STAY, HOBBS, AND BURROWS) 726
- Research needed on electrical contacts, 804
- RICKETT, R.: *Discussion on Grain Growth in Metals Caused by Diffusion*, 400
- Riveting: aluminum, 147
- monel metal and nickel, 87
- ROBERTS, E. H., MORGEN, R. A., SWENSON, L. G. AND NIX, F. C.: *Ternary Systems of Lead-antimony and a Third Constituent*, 316
- ROLLE, S.: *Discussion on Metal Recovery from Bronze Foundry Slags*, 724
- ROUSH, G. A.: *Discussion on Distribution of Tensile Strength in Hard Drawn Copper Wire*, 542
- S
- ST. JOHN, A.: *Condition of Thorium in Thoriated Tungsten Filament*, 228; *Discussion*, 239
- ST. JOHN, A.: *Discussions: on Twinning in Ferrite*, 459
- on *X-ray Analysis of Plastic Deformation of Zinc*, 274
- St. John X-ray diffractometer, 229
- Sampling and Evaluating Secondary Non-ferrous Metals* (WRIGHT), 672
- Sauveur method of making metallic single crystals, 311
- Schaller and Orbig method of making metallic single crystals, 310
- SCHUMACHER, E. E.: *Discussion on A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 366, 367
- Scrap metal: aluminum: classification, 727
- market prices, 729
- non-ferrous: classification and preparation, 694, 703
- contamination effect and control, 711
- sampling and evaluating, 672
- use in United States, 660, 700
- Secondary metals, non-ferrous (*see also names of metals*): contamination, causes, 711
- contamination of scrap, effect and control, 711
- producers, 700, 702
- production methods, 705
- recovered in United States, 662, 695, 701
- sampling and evaluating, 672
- smelter laboratory important, 708
- sources of "raw" material, 702
- SEIFERT, H. F.: *Classification and Preparation of Non-ferrous Scrap Metal and Alloys*, 694
- Silicon, importance in metallurgy of aluminum, 198
- Silicon-aluminum alloys. *See* Aluminum-silicon
- Silver alloys, etching reagent, 802
- Silver, determination of platinum by spectrum analysis, 305
- Silver-cadmium alloy, hardness, 755
- Silver-copper alloy, equilibrium diagram, 744
- Silver-gold alloy, hardness and internal pressures, 417, 423
- Silver-manganese alloys. *See* Manganese-silver
- Silver, sterling: analysis, 743
- annealing, 746, 756, 758
- casting, 745
- derivation of name, 744
- ductility, 750
- hardness, 746, 750, 755
- melting, 745, 757
- microstructure, 751, 756
- rolling, 746
- tensile strength, 750
- SMITH, C. S.: *Discussions: on Manufacture of Sterling Silver and Some of Its Physical Characteristics*, 756
- on *A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 362
- SMITH, D. M. AND TWYMAN, F.: *Quantitative Spectrum Analysis*, 280
- Sodium, effect on aluminum-silicon alloys, 202

- Soldering: aluminum, 139
monel metal and nickel, 87
- Solders: bismuth effect in, 356
cadmium, in commercial operations, 359
cadmium-zinc, 356, 365
characteristics and requirements, 352
definition of terms alloying and wetting, 362
lead-tin-cadmium, 352
 bibliography, 361
 wetting qualities, 361
lead-tin-cadmium-zinc, solidification ranges, 356
solidification ranges of Pb-Sn-Cd-Zn alloys, 356
tensile strength of joints, 357, 363
tin-lead, antimony content limit, 722
wiping, high-lead alloys good, 366, 367
- Some Aspects of the Commercial Manipulation of Aluminum (NAGEL), 127
- Some Peculiar Results in Hardness Tests of Lead-antimony Alloys (HOWARD), 369
- Specifications, metal, wider use desirable, 710
- Spectrographs, modern, method of using, 284
- Spectrum analysis: bibliography, 303
 comparisn spectra, 287
 development, 280
 four ways of producing radiation for analysis, 284
 nomenclature, 281
 qualitative, value, 280
 quantitative, 280, 288
 specific examples, 292
 visual instrument for estimating percentage of nickel and chromium in steel, 303, 305
- Spinning monel metal and nickel, 86
- STAT, T. D., HOBBS, D. B., AND BURROWS, H. O.: *Remelting Secondary Aluminum*, 726
- Steel: chrome-nickel, heat-treated, endurance limit, 609
 compressibility, 414, 423
 corrosion-fatigue, effect of absorption of hydrogen, 611, 614
 determination of carbon by spectrum analysis, 301
 determination of chromium by spectrum analysis, 300, 303, 305
 determination of manganese by spectrum analysis, 300
 determination of nickel by spectrum analysis, 303, 305
 fatigue and corrosion-fatigue, 577 et seq.
- Stereographic projection method, 430
- Strain-hardening in metallic crystals during deformation by translation, cause, 375
- Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders (SWARTZ) 352
- SWARTZ, C. E.: *A Study of Certain Alloys of the Lead-tin-cadmium System with Reference to Their Use as Solders*, 352; Discussion, 367
- SWEENEY, W. T. AND HIDNERT, P.: *Discussion on Aluminum-beryllium Alloys*, 643
- SWENSON, L. G., MORGEN, R. A., NIX, F. C. AND ROBERTS, E. H.: *Ternary Systems of Lead-antimony and a Third Constituent*, 316
- T
- Tammann method of making metallic single crystals, 307
- TARASOV, P. P.: *Discussion of Condition of Thorium in Thoriated Tungsten Filament*, 237
- TEMPLIN, R. L.: *Machining Aluminum*, 149; Discussion, 163
 Discussion on Corrosion of Metals as Affected by Time and by Cyclic Stress, 610
- Ternary Systems of Lead-antimony and a Third Constituent (MORGEN, SWENSON, NIX AND ROBERTS) 316
- Terne drosses, skims and ashes, sampling and evaluating, 683, 693
- THIEME, C. O.: *The Contamination of Metal Scrap, Its Effect on the Value, and Suggested Means of Control*, 711; Discussion, 720
 Discussions: on Metal Recovery from Bronze Foundry Slags, 724
 on Modern Non-ferrous Secondary Metal Producer, 709
 on Sampling and Evaluating Secondary Non-ferrous Metals, 693
- Thoria: melting point, 237
 presence in tungsten metal, 237, 239
- Thoriated tungsten filament: amount of dissolved thorium, X-ray analysis, 235
 condition of thorium, X-ray analysis, 228, 238, 239
- Thorium: amount dissolved in tungsten filament, X-ray analysis, 235
 condition in thoriated tungsten filament, X-ray analysis, 228, 238, 239
 melting point, 237
- THUM, E. E.: *Discussion on Metal Recovery from Bronze Foundry Slags*, 725
- Tin: determination of antimony by spectrum analysis, 299
 effect in solders, 364
 in ternary diagrams, 316
- Tin drosses, skims and ashes, sampling and evaluating, 683, 693
- Tin, secondary: recovery in United States, in 1910-26, 663 et seq.
 in 1924-25, 695
 in 1925, 701
- TREWIN, C. S.: *Wrought Zinc*, 95
- Tubing: aluminum strong alloys, 113
 gas-welded, monel metal, sizes and uses, 92
 seamless: aluminum, sizes, 107
 nickel, sizes and uses, 92
- Tungsten. See Thoriated
- Twinning. See Crystals—of all metals
- Twinning in Beryllium, Magnesium, Zinc and Cadmium (MATHEWSON AND PHILLIPS) 445
- Twinning in Copper and Brass (PHILLIPS) 429

- Twinning in Ferrite* (McKEEHAN) 453
Twinning in Metals (MATHEWSON) 7
 TWYMAN, F. AND SMITH, D. M.: *Quantitative Spectrum Analysis*, 280
 Type metal, expansion on solidifying, 373

U

- Use of the Noble Metals for Electrical Contacts* (KINGSBURY) 804

V

- VACHER, H. C. AND JORDAN, L.: *Discussion on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 564
 Vacuum-pouring, 783, 784
 Van Arkel method of making metallic single crystals, 309
 VAN LIEMPT, J. A. M.: *The Production of Metallic Single Crystals*, 307; *Discussion*, 315
 van Liempt electrolytic method of producing metallic single crystals, 310

W

- Waste material. *See* Scrap Metal; Secondary Metals
 WATERFIELD, J. B.: *Discussions: on Contamination of Metal Scrap*, 719
 on Manufacture of Sterling Silver and Some of Its Physical Properties, 756
 on Modern Non-ferrous Secondary Metal Producer, 710
 WEBSTER, W. K.: *Discussion on Physical Characteristics of Commercial Copper-Zinc Alloys*, 71, 73
 Welding: aluminum, 140, 148
 monel metal and nickel, 87
 WICHERS, E.: *Discussions: on The Platinum Metals and Their Alloys*, 782
 on Use of the Noble Metals for Electrical Contacts, 823
 WILSON, T. A.: *Discussion on X-ray Analysis of Plastic Deformation of Zinc*, 277
 WILSON, T. A. AND HOYT, S. L.: *X-ray Analysis of Plastic Deformation of Zinc*, 241
 Wire: copper (*see* Copper Wire)
 monel metal and nickel, sizes and uses, 89
 WISE, E. M.: *Discussions: on Alpha Phase Boundary of the Copper-nickel-tin System*, 514
 on Distribution of Tensile Strength in Hard Drawn Copper Wire, 540

- Wise, E. M.: *Discussions: on Gold, Silver, Copper Alloys*, 802
 on Manufacture of Sterling Silver and Some of Its Physical Properties, 757
 on The Platinum Metals and Their Alloys, 783, 785
 WITHERELL, C. S.: *Discussions: on Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 566
 on Sampling and Evaluating Secondary Non-ferrous Metals, 691
 WRIGHT, T. A.: *Sampling and Evaluating Secondary Non-ferrous Metals*, 672; *Discussion*, 688, 692, 693
 Wrought Zinc (TREWEN) 95

X

- X-ray Analysis of Plastic Deformation of Zinc* (WILSON AND HOYT) 241
 X-ray diffractometer, St. John, 229

Y

- Y alloy. *See* aluminum Alloys

Z

- ZIEGLER, N. A. AND BRACE, P. H.: *Application of a High-vacuum Induction Furnace to the Study of Gases in Metals*, 544; *Discussion*, 570
 Zinc: determination of small quantities of cadmium, lead and iron by spectrum analysis, 292
 drawing, directions for, 98
 effect in solders, 356, 364, 367
 plastic deformation (*see also* *Crystals, Zinc*):
 investigation of theories, 241, 272, 276
 review of work done, 241
 X-ray analysis, 241, 269
 rolled, testing, 96
 strip, for automatic forming operations, 97
 wrought, commercial forms, 95
 Zinc alloys, secondary recovery. *See* Zinc Secondary
 Zinc ashes, drosses and skimmings, sampling and evaluating, 684
 Zinc crystals. *See* Crystals, Zinc
 Zinc, secondary: recovery in United States, in 1910-26, 663 et seq.
 in 1924-25, 695
 in 1925, 701
 shapes, 707

PROPERTY
OF
HANDY & HARRMAN